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The Journal of Industrial and Engineering Chemistry

PUBLISHED BY

The American Chemical Society

VOLUME XII, 1920

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The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY
AT ESCHENBACH PRINTING COMPANY, EASTON, PA.

Volume XII JANUARY 1, 1920 No. 1

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Published monthly. Subscription price to non-members of the American Chemical Society, $6.00 yearly; single copy, 60 cents
Price per single copy to American Chemical Society members, 50 cents. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted
Entered as Second-class Matter December 19, 1908, at the Post Office at Easton, Pa., under the Act of March 3, 1879
Acceptance for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized July 13, 1918

All communications should be sent to The Journal of Industrial and Engineering Chemistry
Telephone: Vanderbilt 1930 **Cable Address: Jiechem** **35 East 41st Street, New York City**
Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Secretary, 1709 G Street, N. W., Washington, D. C.

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EDITORIALS

OFFICERS FOR 1920

This space has been reserved for a last minute message from Secretary Parsons giving the names of the officers elected for the year 1920. A telegram received just before going to press announces the following:

President
W. A. Noyes

Directors
Wilder D. Bancroft
A. D. Little

Councilors-at-Large
Irving Langmuir
Wm. McPherson
S. W. Parr
M. C. Whitaker

CHEMICAL WARFARE SERVICE ENDANGERED

The House of Representatives is about to fly the track. No, that statement is too broad; confine it to the House Committee on Military Affairs. Reliable information reaches us that in the House bill, now being drafted, for the reorganization of the Army, the Chemical Warfare Service is to be made a subordinate division of Ordnance.

This is a most surprising development. A few weeks ago there seemed to be a practically unanimous opinion among members of Congress that this Service should be a separate and distinct unit of the War Department. This opinion was confirmed by a statement of Hon. Julius Kahn, Chairman of the House Committee on Military Affairs, reported in the *Congressional Record* of November 15, 1919, p. 9061. Among other things, he said:

> It is believed by the members of the committee that in the legislation that we will ultimately report to the House such branches of the Army as a tank section and a chemical warfare section will have to be provided. These are two of the entirely new developments of modern warfare.

This important pronouncement was given wide publicity by the Washington correspondents of the daily press as forecasting the probable outline of the bill soon to be reported by the Committee. Then Mr. Kahn was called to California.

There were further grounds for the conviction that all was going well as to the Chemical Warfare Service. On November 22, 1919, the Annual Report of the Chief of Staff was issued and in this report General March, with the hospital reports before him, announced that gas warfare had been proved humane. Evidently the General has learned well the execution of that feature of military tactics known at one time as "Right about, face!" And then on December 18, 1919, the Washington correspondent of the New York *Evening Sun* sent to that publication a lengthy special dispatch, evidently written with authorization, outlining the general features of the bill for the reorganization of the Army, now being drafted by a subcommittee of the Senate. One of the features of this bill, according to the correspondent, will be "establishment of the Chemical Warfare Service as a separate branch of the Army." This information we had received from other sources.

Was ever a legislative matter in prettier shape than this seemed to be? The original plan of the General Staff had been to bury the Chemical Warfare Service by making it a subordinate division of the Engineer Corps. This move, however, seemed to have been upset completely by the overwhelming conviction among members of Congress that there should be a separate and distinct unit. Now comes out of Washington the reliably confirmed report that under the acting chairmanship of Representative D. R. Anthony, Jr., of Kansas, the House Committee is drafting a bill in which this Service is to be made a subordinate division of Ordnance, not upon the grounds originally set forth by Secretary Baker and General March, in recommending its minimization as a branch of the Engineer Corps, but *for reasons of economy*. As we try to trace the origin of this new movement, invariably we hear that the General Staff is responsible for it. The old determination to smother this Service still exists; there is proposed only a shift in its location, and this proposal is cloaked under the specious argument of economy.

We are not willing to believe that a majority of the House would accept any such recommendation. Ordnance itself does not desire it. This is attested by the words of General Pershing. His testimony before the Joint Committee of the House and Senate was as follows:

> I think it [Chemical Warfare Service] should be developed, and it would be developed better under a separate organization than under any other bureau. There is no doubt about that.
>
> The Chief of Ordnance does not know anything about it, and he does not want it, as far as that is concerned. The Chief of Ordnance, I have no doubt, would give to it every attention. But it is not in his line, and he could not give it the attention that it should be given; he would not draw to his aid the chemists of the country so readily as some man who had been closely associated with the Chemical Warfare Service would do. That is a very important matter, because it would be a department of investigation.

As to economy, we fail to see the point. One thing is certain: Failure to make the Service a separate unit will deaden the coöperative spirit among the civilian chemists of the country. General Sibert and Colonel Fries are right when they estimate this coöperation at so high a value. It can readily be obtained and without cost, but the chemists of the country must feel that they are engaged upon something which Congress considers worth while. General March, in his Annual Report, gives the clinching argument in favor of a highly developed Chemical Warfare Service. He points out that the chief lesson of the war is the necessity of having the nation so organized in peace that its entire resources may be instantly and effectively mobilized for war. Then he adds:

This consideration accentuates the necessity of a War Department organization in future which is adequate to efficient formulation and execution of a military program, which will require a definite and effective articulation of the War Department with all the agencies involved in the mobilization of the industries, activities, utilities and resources of the nation.

If, however, the General Staff is set upon the elimination of the Chemical Warfare Service, then let it be turned over to the Navy, for we are confident that that Department will do well by it, as it does by everything else it undertakes.

We cannot afford to take chances in so important a matter; nor, in justice to the men who will have to fight our future battles, can we afford a niggardly policy in its development. Recently we have talked with leaders of thought among American, French and British officers and found unanimity of opinion that chemical warfare is to play a greater and still greater rôle in the future. If we lag behind in this respect we assume a responsibility which some day may cover us with regrets and reproaches.

How can this unfortunate move in the House Committee be met? This is a democracy and Congress is representative of the public thought of the country. Stir up that thought and let it find its way to Washington. Responsibility in this matter rests primarily upon us. Our membership reaches into every Congressional district. It is time to get into the saddle again and to do so quickly. Let our people and our Congressmen know what this new move means.

KICKING UP DUST

These are the days when importers and dealers in dyestuffs are busy, very busy—not in matters of merchandising but in the political game of kicking up dust. The Longworth bill is now before the Senate Committee on Finance, an early report is expected, and doubtless the Senate will take action quickly. Importers and dealers know, just as well as manufacturers do, that the enactment of a dye licensing system will insure the successful development of the American industry. This means only one thing to the importer or dealer—"Get another job." Evidently they think it is the time to cloud the issue in every way possible. Here is the way the dust is kicked up.

First, an importer or a dealer starts a loud howl, anonymously, that a license system will lead to monopoly. Immediately afterward there is started a batch of rumors that this or that firm is going to absorb such and such other firm. Officials of both firms issue positive denials, and characterize the rumors as ridiculous and absurd. Meanwhile the same dust is raised in another part of the lot, or perhaps the rumor is switched to another set of well-known dye manufacturers. Our telephone has been kept busy for the last week with requests from trade papers for information concerning the correctness of such rumors. We have a standard reply as follows: "If you will trace that report to its origin you'll find that it was started by an importer or a dealer." In every case the reply comes back: "You are right, we have already traced it, but we just wanted your opinion." Then we close the conversation by remarking: "Why do you want to waste your time and energy on that silly stuff, the motive of which is so easily recognizable?" But the next day the telephone rings again and the conversation is repeated. Dust raising pure and simple!

During the next few weeks the trade papers of New York City are going to be put severely to the test, in their legitimate eagerness to print the news, as to whether they are mere gossip bags or real exponents of American industrial progress. We believe that they will meet that test fully and cleanly.

Sometimes, however, the dust raisers in their desperation flop into a mud hole and then deliberate effort is made to befoul whomsoever may be the object of attack. For instance, we have seen a printed statement recently and friends have brought us reports of conversations in which the charge was made that, while nominally working for the public and common good and in an official representative capacity, we have been really seeking to serve private interests; just how no one specifies, and the mud-flingers are very careful to go just far enough to avoid a libelous statement. These statements do not bother us for a minute. We have ample confidence in the fair-mindedness of the average American citizen, and when all the facts are known about the vat dye situation, as they soon will be known, the mud-flingers will then realize that their splotches have not scattered but have gone straight up into the air, only to return upon their own heads.

Then there are the burrowers. Not content with disturbance of the fair face of the earth through agitation of the dust and mud, they work in subterranean channels. The Alien Property Custodian, in his testimony before the subcommittee of the Senate Committee on Finance, read an interesting document into the record. Just a bit of history first to enable a full understanding of the document. On October 4, 1919, just two weeks after we had settled down in Paris, there had been secured proposals which would have covered the needs of all American consumers of vat dyes for the next six months. It remained only for some authorized body to close the deal. Meanwhile the allocation certificates had been issued to individual consumers to import through any commercial channel. Confusion and delay ensued. Gradually it was realized that by uniting upon the Textile Alliance, Inc., which had been designated by the State Department to receive the Reparation dyes, quick action and very reasonable prices could be obtained. Mr. Metz saw this and at once assigned to the Textile Alliance all of the allocation certificates which had been turned over to him. The case was different with Kuttroff, Pickhardt & Co., who held a large number of these certificates, turned over to them by consumers. Only on request of individual consumers did they assign their certificates to the Textile Alliance. This meant more delay, but by the middle of November practically all had been assigned. It was indeed surprising when the Alien Property Custodian read into the record at the hearing the following cablegram:

> "14 NOVEMBER
>
> ANILIN FABRIK, LUDWIGSHAFEN.
>
> We fully expect modification Government regulations which will permit us to confirm our order. This will enable you to maintain your position that all goods to this country outside reparation goods should come to us.
>
> PURPURINE (KUTTROFF-PICKHARDT)"

Of course, no change of policy was in contemplation by the War Trade Board. The intent of the cable was all too plain, and on November 25, 1919, we received a cable from Frankfort, Germany, indicating that it would be impossible to extend further the agreement made at Versailles on October 4, 1919. This cable was at once turned over to the State Department, whose officials refused to acknowledge it as a cancellation and immediately entered emphatic protest with full reasons therefor. Sequel: On December 15, 1919, we received the following cablegram:

> "FRANKFURT MAIN, Dec. 15.
>
> "CHARLES HERTY,
> "35 East 41st Street, N. Y.
>
> "Have pleasure informing you that I have succeeded prolongation option as given you fourth October. For all details are ready negotiate with your representative Stephenson Paris.
>
> VON WEINBERG."

The burrowers had been at work, they had worked in vain, and the evidences of their burrowing are a part of official records. Doubtless these subterranean operations will be continued, but our prediction is that consumers of dyestuffs, when all the facts are known to them, will turn their heads in disgust from all such earth-movers, whether they be dust-kickers, mud-flingers or burrowers.

A HOUSE BUILT UPON A ROCK

For many months we have been endeavoring to reach a definite legislative policy regarding two questions which are intimately bound up with the future welfare and security of the nation—the integral character of the Chemical Warfare Service in the reorganization of the Army, and the protection of its logical reserve, the dye industry. The fight for national safety along these lines has been a long one; but during its progress the masses of our people have been undergoing a steady education through the columns of a thoroughly sympathetic press.

Right here is the chief difference we have noted between conditions in America and in other countries. In the latter, for example France, it has been easy to secure governmental coöperation and the enactment of favorable legislation—so easy indeed that it leads to the apprehension that such conditions may prove a house built upon the sand. With us it has been a prolonged struggle, but out of that very struggle has come the strength of popular understanding and sympathetic support, the bed-rock foundation of a permanent policy which no sudden shift of official thought can damage, or, by chance, sweep away.

The columns of the daily press furnish a true index of the extent of this campaign of popular education. For two months we scanned closely the columns of the French papers for articles on subjects connected with chemistry, and rarely was the search rewarded. Then in memory we could see the mass of newspaper clippings pouring into the office of the A. C. S. News Service from every state in the Union. The contrast forced the convincing thought that America is slowly but surely on the road to certainty and to permanency in these matters; slowly, because of the necessarily slow processes of public education, but surely, because of its solid foundation.

This campaign of popular education through the press, constantly increasing in extent, has resulted chiefly from the work of the SOCIETY'S News Service under the technical direction of that experienced newspaperman, Mr. John Walker Harrington, who was selected just a year ago to carry on this important public responsibility which inherently belongs to an organization so truly national as the AMERICAN CHEMICAL SOCIETY.

In the next issue we hope to present some of the important results of this work which made so deep an impression upon the Directors that they approved an increased budget for this purpose during the year 1920. In advance of this showing, however, two developments of the past year are especially to be noted.

First: Publicity work in connection with the general meetings has frequently suffered because of lack of continuity between the general work carried on throughout the year by the SOCIETY and that done by the local committee at the time of the general meetings. The Philadelphia Section overcame this difficulty at the last general meeting by securing, at its own expense, the services of Mr. Harrington, and placing the entire matter of publicity in his hands, he acting, of course, in coöperation with the publicity committee of the Section. The result was astonishing. The space given to that meeting by the press throughout the country was incomparably greater than had been given to former meetings. The Directors have now appropriated funds to secure the services of Mr. Harrington for each of the general meetings in 1920. This will leave upon the local sections only the expenses of room rent, stenographic assistance, and material supplies.

Second: A most interesting feature has been the coöperation of Mr. Harrington with local sections in advising as to methods and details of securing the interest of the local press in the activities of the local sections. A special group of clippings shows how successful this has been in those sections where coöperation was attempted. The work was carried on largely by correspondence and it is believed that its enlargement will prove one of the features of the new year. Whenever his aid is desired it may be counted on.

ORIGINAL PAPERS

THE COMMERCIAL OXIDATION OF AMMONIA[1]

By George Arthur Perley
New Hampshire College, Durham, New Hampshire

Received September 4, 1919

A vast number of articles have appeared from time to time during recent years covering various phases of the work involved in the production of nitric acid by means of ammonia oxidation. Most articles refer to the historic observations by Kuhlman in 1839 and then trace the slow developments which include the patent of Tessié du Motay in 1871 and the work of Ostwald in 1900. This interesting historical development has been so well covered in previous papers that no effort will be made to cover the bibliography of the subject. Excellent bibliographies may be found in various publications.[2] Several recent articles have appeared on this subject.[3]

TERMINOLOGY

Many apparently conflicting statements have appeared in some of the previous publications, yet some of these can be reconciled by a more careful statement of conditions and facts. Up to the present time there have been no attempts at standardization of methods or nomenclature, and this alone has been accountable for a certain number of errors. The catalyst chamber is known as a converter, a tower, a burner, a furnace, an oxidizer, etc., while the catalyst itself has been variously termed a screen, a net, or a gauze. A serious misunderstanding has resulted from a failure to express the capacity factors in understandable terms. Much of the ammonia oxidation work has been carried out with multiple layers of a platinum, or platinum alloy gauze, and the yields or gas flows have been expressed in terms of cubic feet of the ammonia-air mixture per square foot of gauze surface. In one instance an author has referred his yields to the surface area of the first layer of exposed gauze, while another has considered the surfaces of all of the separate layers. It is all folly to attempt advancement along these lines of activities unless every one will consider capacities in respect to the actual pounds (unit weight) of ammonia catalyzed to nitric oxide per unit weight, or ounces of platinum gauze or other catalyst. If it is not convenient to express the velocity, or space-time data, for such work, the future publications should at least be quite explicit as to the relationship of the gas flows in unit time to the total surface area of the catalyst employed.

The grade of ammonia which has been utilized in previous work has varied between wide limits, and no apparent attempts have been made to publish the complete data upon the exact composition of the gas mixtures which were oxidized. The ammonia oxidation reaction does not proceed to nitric oxide at any appreciable rate in the absence of a catalyst at even 800° C. As the history of contact or catalyst poisons is well known, it seems rather sad that previous publications and experimental research have not established their "zero setting" by the use of the purest type of ammonia available (or at least have not used anhydrous for scientific research). The least that could be expected of a publication should be an exact statement of the gas composition which was employed. As evidence of this state of affairs a case may be cited with which the writer is familiar. An unfortunate misunderstanding came about through the failure to establish the exact quality of gas which was being oxidized. The situation arose over the possible presence of certain phosphorus compounds within the ammonia-gas mixture. Even to-day a difference of opinion exists in reference to the various statements which have been made relative to the action of phosphorus compounds as catalytic poisons in the ammonia oxidation reaction. This is essentially due to the fact that no analytical methods were perfected, or adopted, to distinguish between phosphorus which was present as phosphine and that which was present as a more stable form. Unfortunately, this is not the only case where failure to standardize the analytical procedures has caused unfortunate misunderstandings. A similar state of affairs has existed in reference to the standardization of the methods of sampling, the analytical procedures and the catalyst temperature measurements.

The above matter has perhaps been treated in too great detail, but it is to be desired that greater care in standardization be secured in the future and thus prevent a repetition of some of the past misunderstandings and inaccuracies.

STABILITY OF INTERMEDIATE COMPOUNDS—The theoretical foundations involved in the production of nitric acid by means of the oxidation of ammonia are well understood. However, it may not be amiss briefly to review the fundamental features in this young and important industry. It is true that Ostwald[1] had developed his ideas as to the law of successive reactions at about the period when he was working on the oxidation of ammonia. We realize the importance of the fact that when there is the possible formation of a consecutive series of intermediate compounds, that compound which involves the smallest loss of free energy will be formed first, then the one involving the next smallest loss will come second. The proof of the existence of the intermediate stages depends upon the stability of those compounds under the given conditions. In the early work of Ostwald, the formation of the possible intermediate nitrogen oxides was recognized merely as a step to the final nitrogen. He realized that the function of the catalyst was towards the selective increase in velocity of one reaction. His views as to the desirability of removing the oxygen compounds rapidly from the zone of reaction, through a very short contact time, were stated, but very badly qualified.

---

[1] An abstract of this paper was read before the Division of Physical and Inorganic Chemistry, 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

[2] "Literature of the Nitrogen Industries 1912–1916," Helen R. Hosmer, THIS JOURNAL, **9** (1917), 424; John C. Boyce, *Chem. & Met. Eng.*, **17** (1917), 228; "How the Nitrogen Problem Has Been Solved," H. J. M. Creighton, *J. Frank. Inst.*, **187** (1919), 705, 733.

[3] "The Oxidation of Ammonia," W. S. Landis, *Chem. & Met. Eng.*, **20** (1919), 470; "Commercial Oxidation of Ammonia to Nitric Acid," C. L. Parsons, THIS JOURNAL, **11** (1919), 541; "Analytical Method for Determining Efficiency of Ammonia Oxidation," D. P. Gaillard, *Ibid.*, **11** (1919), 745.

[1] *Z. physik. Chem.*, **22** (1897), 306.

The recent work of Lewis and Adams[1] on "The Free Energy of Nitrogen Compounds," as well as their related publications on oxygen and water, enables us to establish the quantitative relationships which can thermodynamically exist. They give us the values

NH_3 $\Delta F^\circ = -10700 + 5.5\ T \log T - 0.001175\ T^2 - 11.0\ T$
O_2 $\Delta F^\circ = 34600 + 2.75\ T \log T - 0.0028\ T^2 + 0.00000031\ T^3 - 22.4\ T$
NO $\Delta F^\circ = -21600 - 2.50\ T$
NO_2 $\Delta F^\circ = 10200 + 2.75\ T \log T - 0.0028\ T^2 + 0.00000031\ T^3 - 2.2\ T$
H_2O $\Delta F^\circ = -57410 + 0.94\ T \log T + 0.00165\ T^2 - 0.00000037\ T^3 - 3.66\ T$

The analogy to the burning of carbon is most interesting. It has been considered that even at white heat coal burns completely to carbon dioxide when the air is at a high velocity. Yet the equilibrium indicates that at all temperatures above 800° C. the carbon monoxide should be the chief constituent of the gas mixture. There are, however, some differences of opinion relative to this viewpoint. Oxygen seldom reacts by a primary decomposition of its molecule into two atoms. The first product which usually forms when a substance burns contains the whole oxygen molecule.[2] A discussion of this particular phase will be considered separately in connection with some studies upon the reaction velocity-catalyst surface effects.

As far as Ostwald's work was concerned, it may be said that he was successful in isolating his intermediate compound. Thus were established the facts that platinum sponge would favor the velocity of certain of the intermediate reactions occurring in the ultimate oxidation of ammonia, and that the ratios of gas space to contact surface to time were very important features. The close relationship of these factors to the temperature-oxygen variables was not quite clearly stated.

The equilibrium conditions existing between $N_2 + O_2 \rightleftarrows 2NO$ have been carefully investigated by Nernst,[3] while the dissociation of $2NO_2 \rightleftarrows 2NO + O_2$ had been well discussed prior to Ostwald's work by Richardson.[4] It was shown by this last mentioned work that at 760 mm. there was complete decomposition of NO_2 into NO and O_2 at 619.5° C., and that this is a reversible change. The above decomposition of NO_2 begins at 140° C. Jellinek[5] has studied the influence of temperature upon the velocity of the decomposition of NO, and this data shows the quantitative relationships which exist as far as the temperature stability of the intermediate products of the ammonia oxidation reaction are concerned.

It was shown that NO was formed exceedingly slowly at temperatures below 1827° C., yet the rate of the decomposition of NO, in the absence of a catalyst, is at least slow below 1227° C. It is very apparent that if we disregard any possible catalytic influence of the platinum we can commercially work at ranges up to 1227° C. without fear of loss of NO from this reaction. However, this assumption, as applied to the oxidation reaction, is probably not well founded, since the work of Jellinek in platinum tubes between 689° C. and 1387° C. showed a powerful catalytic action of platinum at this temperature range. The necessity of a study of the influence of catalysts upon this decomposition reaction as applied to the ammonia oxidation reaction is quite clear.[1]

It was recognized that the theoretically possible reactions which might exist when ammonia was oxidized could include:

$$4NH_3 + 8O_2 = 4HNO_3 + 4H_2O \quad (1)$$
$$4NH_3 + 7O_2 = 4NO_2 + 6H_2O \quad (2)$$
$$4NH_3 + 5O_2 = 4NO + 6H_2O \quad (3)$$
$$4NH_3 + 3O_2 = 2N_2 + 6H_2O \quad (4)$$

The possible side reactions include:

$$2NO_2 \rightleftarrows 2NO + O_2 \quad (5)$$
$$2NO \rightleftarrows N_2 + O_2 \quad (6)$$
$$4NH_3 + 6NO = 5N_2 + 6H_2O \quad (7)$$

The original passage of a mixture of ammonia and air over platinum sponge had experimentally indicated a strongly exothermic reaction. As the catalyst temperature had at least been above 650° C., it has seemed wise to consider Reactions 3, 4 and 7 as those worthy of closest study for the present.

HEAT CONSERVATION—We have seen that the work of Ostwald resulted in the development of commercial apparatus in which the time of contact of the gases with the catalyst was small and thereby prevented excessive formation of nitrogen, and resultantly poor oxidation efficiencies. The ready decomposition of ammonia had also been considered prior to Ostwald's work by W. Ramsay and S. Young,[2] yet this work did not include air mixtures.

The use of a heat interchanging equipment was adopted by Ostwald for the ammonia-air mixture, and the transfer of a certain quantity of heat was secured from the products of the oxidation reaction. The available illustrations of the type of interchanger which was utilized indicate that the velocity of the ammonia-air mixture was sufficiently low to give a contact time on the interchange surface which promoted a certain decomposition of the ammonia. There is abundance of evidence which shows that there is a serious decomposition of ammonia by almost all bodies except silica at the temperature of the gases resulting from the oxidation reaction; and silica is

---

[1] *J. Am. Chem. Soc.*, **37** (1915), 2308.

[2] *Z. Elektrochem.*, **7** (1901), 446, 447.

[3] *Z. anorg. Chem.*, **49** (1906), 213.

[4] *J. Chem. Soc.*, **51** (1887), 397.

[5] *Z. anorg. Chem.*, **49** (1906), 229. The data of page *272* has a bearing on the ammonia oxidation work.

T°	t° C.	t'	At atmospheric pressure Time for half of decomposition $NO \longrightarrow {}^1/_2N_2 + {}^1/_2 O_2$
900	627	$7.35.10^3$	123 hrs.
1100	827	$5.80.10^2$	10 hrs.
1300	1027	$4.43.10^1$	44 min.
1500	1227	3.30	3 min.
1700	1427	$2.47.10^{-1}$	15 sec.
1900	1627	$1.74.10^{-2}$	1 sec.
2100	1827	$1.21.10^{-3}$	0.07 sec.

[1] *Helvetica Chimica Acta*, **1** (1918), 33.

[2] "The Decomposition of Ammonia by Heat," *J. Chem. Soc.*, **45** (1884), 88.

a very poor heat transfer medium. Kaiser's work[1] clearly shows that it is easy to obtain very poor oxidation efficiencies when preheating the ammonia-air mixture without serious regard as to materials of construction or rates of gas flows.

At the time when the Bureau of Mines began a careful study of this whole question in 1916, it was evident that the commercial development had essentially followed the lines so clearly demonstrated by the work of Ostwald. Dr. W. S Landis,[2] of the American Cyanamid Company, had studied the more recent developments in Germany. It is interesting to note that he states: "The writer is certain that on January 1, 1915, with the exception of the old Ostwald plant, there had been nothing new erected in Germany for the oxidation of ammonia." In 1916 Dr. Landis continued the development of the electrically heated single gauze type of catalyst, which had previously given fair results in Germany.

G. Schüphous[3] has published a description of the electrically heated type as used in Germany. The catalyst which was utilized by the American Cyanamid Company bears a striking resemblance to this. It may be recalled that Ostwald had suggested the use of platinum nets or gauzes.

During the initial work upon the oxidation of ammonia in the United States, during 1916 and 1917, there was much discussion as to the type of catalyst to adopt. The officials of the American Cyanamid Company had every confidence in the utilization of an electrically heated iridium-free platinum gauze as a catalyst. At least fairly satisfactory commercial results could be obtained from such an installation. However, to those who were just beginning a study of this problem it seemed most absurd when dealing with such a highly exothermic reaction as the oxidation of ammonia to utilize external heat energy for the maintenance of a proper catalyst temperature. The employment of an electrically heated platinum gauze within a high heat conducting aluminum frame or converter casing seemed theoretically all wrong. The existence of the Ostwald[4] patent as regards the utilization of a direct heat transfer from the hot exit gases to the ammonia-air intake, as well as the knowledge of the ready decomposition of this intake gas mixture by the prevailing temperatures, made the commercial development a rather cautious one.

After working with the electrically heated type of platinum gauze catalyst it became obvious that the major function of this added heat energy involved the speeding up of the rate of reaction. An increase in temperature should make it possible to oxidize unit quantity of ammonia in a much shorter catalyst contact time. The less this contact time the better becomes the opportunity of preventing the catalytic decomposition of the desired intermediate compounds.

The developments of the early work by the Bureau of Mines has been briefly published.[1] An effort was made by the Bureau of Mines to produce a catalyst and converter equipment which would promote the greatest conservation of heat within the catalyst itself.

The rôle of temperature, contact surface, free space, reaction velocity relationships, oxygen concentration, ammonia decomposition, and poisons, were all recognized as important. Unfortunately, only one of the above independent variables could be studied at a time, and the one most promising of an early solution seemed to be that of the temperature. Could some sort of a catalyst element be devised which would eliminate the use of external heat energy without the uncertain decomposition of the ammonia of the intake mixture? The use of a heat interchanger on the incoming gas has caused all sorts of unsatisfactory results, according to the previous published work. Only meager information was available as to the use of multiple layers of gauzes up to 1917.

THEORETICAL TEMPERATURE INFLUENCE—The theoretical influence of temperature upon the ammonia oxidation reaction has been well discussed. By the application of the law of mass action to the homogeneous system

$$4NH_3 + 5O_2 \rightleftarrows 4NO + 6H_2O \qquad (3)$$

we have

$$\frac{(P_{NO})^4\ (P_{H_2O})^6}{(P_{NH_3})^4\ (P_{O_2})^5} = K \qquad (8)$$

where (P_{NO}), (P_{H_2O}), (P_{NH_3}) and (P_{O_2}) refer to the partial pressures. This equilibrium coefficient K is independent of the relative proportions of the reacting bodies, but it is constant only for a given temperature. This equation by itself only enables one to determine the influence of changes in concentration at a constant temperature.

As applied to this specific reaction, we may assume that an initial one gram molecule of ammonia is employed. x parts of this gram molecule are oxidized to NO by means of an initial quantity of y gram molecules of oxygen. We would have at equilibrium

$1 - x$ gram mols. NH_3
x gram mols. NO
$y - {}^5/_4\,x$ gram mols. O_2
${}^6/_4\,x$ gram mols. H_2O
z gram mols. N_2 (if air was the source of the O_2)

The total gram mols. present at equilibrium are

$$1 - x + x + 1.5x + y - 1.25x + z$$

or

$$1 + 0.25x + y + z$$

and we may call this G.

Equation 8 can then be rewritten as

$$\frac{\left(\frac{x}{G}\,P\right)^4 \left(\frac{1.5x}{G}\,P\right)^6}{\left(\frac{1-x}{G}\,P\right)^4 \left(\frac{y-1.25x}{G}\,P\right)^5} = K$$

or

$$\frac{(x^4)}{(1-x)^4}\ \frac{(1.5x)^6}{(y-1.25x)^5} \times \frac{P}{G} = K$$

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[1] Brit. Patent 24,035 (1911); *Chem.-Ztg.*, **40** (1916), 14.

[2] *Chem. & Met. Eng.*, **20** (1919), 470.

[3] *Metall und Erz*, **13** (1916), 21.

[4] U. S. Patent 858,904 (1907).

[1] C. L. Parsons, *Loc. cit.*

where P = the total pressure.

This is simplified by considering

$$G = 1.25 + y + z,$$

as x is small compared to the other values and nearly constant.

$$\frac{(x^4)\ (1.5x)^6\ (P)}{(1-x)^4\ (y-1.25x)^5\ (1.25+y+z)} = K \qquad (10)$$

However, the change of K with the temperature is the interesting feature and this can be determined by van't Hoff's equation for a system at constant volume.

$$\frac{d \log_e K}{dT} = \frac{U}{RT^2}$$

and the integral of this differential equation becomes

$$\log_e K = -\frac{U}{4.571\ T} + C$$

where C is the integration constant. The values of C have been determined by Nernst[1] for many substances. We find in this specific case that

$$C = 3.5 + (1.5 \times 3.6) - 3.3 - (1.25 \times 2.8) = 2.10$$

The value of U may be taken from data upon heats of formation at T^1.

$$\tfrac{1}{2}\ N_2 + 1.5\ H_2 = NH_3 + 10.990 \text{ g. cal.}$$
$$\tfrac{1}{2}\ N_2 + \tfrac{1}{2}\ O_2 = NO - 21,600 \text{ g. cal.}$$
$$1 + 2 + \tfrac{1}{2}\ O_2 = H_2O + 56,940 \text{ g. cal.}$$

and

$$U = -21,980 - 43,200 + 170,820,$$

or

$$4NH_3 + 5\ O_2 = 4\ NO + 6H_2O + 211,280.$$

Then

$$\log_e K = -\frac{211,280}{4.571\ T} + 2.10 \qquad (11)$$

We have the value of K from Equation 10. This can be simplified by applying the equation for atmospheric conditions and with the use of pure oxygen in place of air. By so doing $z = 0$, and $y = 1.25$ if just sufficient oxygen is used as that demanded for the oxidation of ammonia. By the mathematical solution of Equation 11 it is possible to secure values of x for varying values of T. Without going into the final deductions it is interesting to note that for temperatures up to at least 1500° C. the theoretical oxidation of NH_3 to NO is at all times above 99 per cent.

It is also interesting to note that the influence of temperature upon the value of U can be checked. Nernst[2] has studied $N_2 + 3H_2 \rightleftarrows 2NH_3 + U_1$, and up to 1000° C. he has shown that $U_1 = 21,980 + 7.0T + 0.00331T^2 - 2.44T^4 \times 10^{-9}$.

The work of Nernst and Wartenberg[3] covers a study upon

$$2H_2 + O_2 \rightleftarrows 2H_2O + U_2$$

and it is evident that

$$U_2 = 113,880 + 3.5T + 0.0035T^2 - \tfrac{4}{3}\frac{T^3}{10^6} - 0.4\frac{T^4}{10^9}.$$

Nernst[4] has also studied the equilibrium

$$N_2 + O_2 \rightleftarrows 2NO - U_3$$

and has found $U_3 = 43,200$.

As applied to the simplified reaction

$$2NH_3 + 2.5\ O_2 = 2\ NO + 3H_2O + U_o$$

we have

$$U_o = -U_1 - U_3 + \tfrac{3}{2}\ U_2.$$

Therefore, $U_o = -21,980 - 7.0T - 0.0031T^2 + 2.44T^4 \times 10^{-9} + 1.5\left(113880 + 3.5T + 0.0035T^2 - \tfrac{4}{5}\frac{T^3}{10^6} - 0.4\frac{T^4}{10^9}\right) - 43,200$

or

$$U_o = 105,640 - 1.75T + 0.00195T^2 - 2.0T^3 \times 10^{-6} + 1.84T^4 \times 10^{-9}.$$

From this value we find that the heat of reaction at 0° for 4 molecules of NH_3 is 211,280 per cal. We can also determine the change of U with increase in temperature. The above equation is probably inaccurate for temperatures above 1000° C. By assuming given values of T and solving for U we find that U is essentially constant for the lower temperatures.

T	—273° C.	0° C.	650° C.	800° C.	1000° C
U_1..............	105,640	105,357	105,442	105,875	107.272

TEMPERATURE FACTOR DEVELOPMENTS—It seemed quite certain that, as far as the reaction

$$4NH_2 + 5O_2 = 4NO + 6H_2O + 211,280 \text{ g. cal.}$$

was concerned, that an increase in temperature could not decrease the commercial oxidation efficiency. With this theoretical foundation it seemed as if the problem at least first consisted in a study of methods for the conservation of the maximum amount of heat within the catalyst zone. Varied designs of apparatus were made and operated with this point in view. The description and data presented in Dr. C. L. Parsons' paper[1] give one the developments along this line. In brief, it was found that a multi-layer horizontally installed gauze made it possible to oxidize ammonia with a commercial catalyst efficiency of 90 per cent, when oxidizing approximately 0.05 lb. of NH_3 per min. per oz. of platinum. A good work's practice was found to use three layers of gauze of 80 mesh wire, 0.0026 in. diam., and with a combined gas flow of from 20 to 22 cu. ft. per sq. ft. of total gauze surface employed in the three layers. The interesting feature of this first work was involved with the fact that, when using high-grade coke oven aqua ammonia, the use of a multi-layer horizontally installed gauze gave as good commercial results at the same capacity per unit weight of platinum as the single electrically heated gauze. In the early commercial work there were periods when either type seemed to operate poorly, but the knowledge of poisons was exceedingly limited at that time. It was an easy matter to attribute the cause of any troubles to various grades of platinum catalyst employed, for all sorts of gauzes were in use in the early work. There was doubtless a certain error due to the poorer methods of analytical control of the results, yet at the best the percentage error must have been small.

But little emphasis was paid to the grade or source of ammonia. Nevertheless, the facts remained that the use of a flat, horizontally installed multi-layer (3 layers) platinum gauze did not require any external electrical energy for the establishment of fairly satisfactory commercial yields. The Bureau of Mines accumulated much data in making these comparisons, but one particular series will serve to illustrate the case. This is given in Table 1.

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[1] "Theoretische Chemie" **1909**, 708.

[2] *Z. Elektrochem.*, **1910**, 100.

[3] *Z. physik. Chem.*, **56** (1906), 534.

[4] *Z. anorg. Chem.*, **49** (1906), 226.

[1] *Loc. cit.*

Table 1

Grade of NH_3: Coke oven aqua
Platinum catalyst: 0.0026 in. diam., 80 mesh wire

	Per cent
Pt	98.67
Ir	0.28
Rh	1.08
Pd	0.12
Fe	0.32

	Electrically heated.	Three layers horizontally
Number of tests	22	18
Lbs NH_3/min./oz. Pt	0.054	0.06
Average oxidation efficiency, per cent	90.8	91.2
Rate of flow/min./sq. ft. gauze, cu. ft	18	18
Average NH_3 vol. conc., per cent	9.56	11.5
Average NH_3 wt. conc., per cent	5.92	7.19

In either of the above cases an aluminum converter frame was used.[1] The high heat conducting properties of this aluminum converter casing were recognized as theoretically unsound. The importance of this feature was brought home to the writer at a later time when he was studying the oxidation of normal autoclave cyanamide ammonia. The operations referred to were being conducted in cold weather and certain poisonous constituents were present in the gas mixture. A cold wave of air blowing on one side of the aluminum converter caused inactive spots to develop selectively on the cold side of even an electrically heated gauze. This phase will be treated more fully in a later paragraph. In case deleterious substances are present in the gas it appears that an abnormal cooling effect is produced within the catalyst.

Since these observations, this feature has been theoretically discussed by F. G. Liljenroth.[2] The normal method of correcting this fault was by the use of a non-conducting converter casing which could also be lined with a proper refractory.

After several modifications of a heat conserving converter had been actually fabricated and operated, a type of converter as described in the article by Parsons[3] was found to give the results as indicated in the above-mentioned article.

The previously published data refer to the use of a 99.9 per cent Pt gauze upon a high grade of coke oven aqua as the source of NH_3. The improved type of converter was shown to give an average gauze conversion of 90.7 per cent upon a 10.57 per cent NH_3 (by vol.) gas mixture when approximately 0.05 lb. of NH_3 was oxidized per min. per oz. of platinum (using 0.0026 in. diam. wire and 80 mesh gauze). A good operating average capacity for this type of converter was 0.82 lb. of NH_3 per min. for four layers of a platinum gauze catalyst wound in the form of a cylinder 9 in. in diameter by 13 in. high, and weighing 16.5 oz.

The aim in the initial development of a multi-layer cylindrical form of platinum catalyst had been towards the production of a catalyst which would give as good commercial operations as the single-layer electrically heated gauze type of converter. The chief features of the cylindrical form are involved in the efficient cross radiation within the inner zone of the cylinder and the utilization of a non-conducting casing. Although this type of converter could not claim much superior oxidation conversions, at the same capacity, than the converter utilizing electrical energy, yet the elimination of outside energy had been accomplished. It seemed as if this was an important step, since a 12 in. by 24 in. electrically heated gauze type of converter would utilize at least 5 kw. per catalyzer, or 285 k. w. h. per ton HNO_3. For a plant the size of U. S. Nitrate Plant No. 2, this means at least 3500 kw. No claim was made that this converter represented the final word in heat conservation, yet it was a step in the partial solution of one of a dozen problems involved in this work.

Twelve of the cylindrical multi-layer gauze converters were installed in one of the two oxidation units at U. S. Nitrate Plant No. 1. All were never in operation at one time. The comparison of the operation of two electrically heated single-layer and one cylindrical multi-layer (4 layers) type of ammonia catalysts at the plant of the Semet-Solvay Company of Syracuse, N. Y., is given in Table 2.

Table 2—Comparison of Converters as Commercially Operated for Preliminary Tests

		Electrically Heated Landis	Single-layer Syracuse	Cylindrical Multi-layer Syracuse
Surface of exposed layer, inches		12 × 24	12 × 24	11.5 × 9 diam.
Size of gauze, inches		13 × 27	13 × 27	13 × 114
Number of layers		One	One	Four
Appearance		Flat Rect.	Flat Rect.	Cylinder, 9x12
Size of wire in gauze, inches		0.003	0.0026	0.0026
Total weight of platinum, ounces		5.20	3.11	16.50
NH_3 oxid. per min., lbs		0.17	0.15	0.81
NH_3/oz. Pt./day, lbs		46.2	68.3	70.70
Total cu. ft. gas per min		42	44	180–190
Electrical energy in kw		5	6	None
NH_3 concentration	per cent by vol.	9	9–10	10–11
	per cent by wt.	5	5–6	6–7
Gauze temp., deg. C		685	750	780
Oxidation efficiency, per cent		91–92	90.8	90.7
Cost of one converter		$227.11	.....	$308.50
Cost of electrical equipment		$187.30	.....	None

There is some difference of opinion as to the influence of size of diameter of the wire gauze. It has been difficult to draw fine conclusions in respect to this feature on a commercial scale, since the early work was handicapped by the lack of absolutely accurate methods of gas flow measurements. The recommendation of Dr. Landis for the use of a 0.003 in. diameter wire for a single-layer type of catalyst was probably well taken in the case of the oxidation of cyanamide ammonia. When this gauze is fabricated of absolutely pure platinum the greater rigidity of the 0.003 in. diameter wire gauze over the 0.0026 in. probably yields a higher percentage length of life for the catalyst. It was found most difficult to define the difference in the commercial capacities of these two types of gauze as referred to actual total surface of exposed gauze. However, the comparison as to capacities per unit weight was quite clear.

As applied to the proposed U. S. Nitrate Plant No. 1 installation, for the oxidation of 32,486 lbs. of NH_3 per day, the data of Table 2 can be revised to that of Table 3.

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[1] C. L. Parsons, *Loc. cit.*, Fig. 6.

[2] *Chem. & Met. Eng.*, **19** (1919), 287.

[3] *Loc. cit.*, Fig. 7.

TABLE 3

	Cylindrical Multi-layer Type	Electrically Heated Laodis Type
Number converters required	24	130
Total wt. of platinum, ounces	396	676
NH_3 per day per converter, lbs.	1250	250
HNO_3/day/converter at 90 per cent, lbs.	4175	835
Total kw. hr. per year	None	5,694,000
Total converter cost	$7404	$29,524.30
Total elect. equip. cost	None	$24,349.00
Total floor space in sq. ft.	766	5460

Assuming the same oxidation efficiency and labor charges, the above table indicates that for a plant whose source of NH_3 was that of Grade A aqua, or its equivalent, the added cost for electrically installed converters would be

Extra converters	$46,469.00
Extra building	14,000.00
Extra platinum	28,000.00
Total extra installation costs	$88,469.00

If we consider a $17^1/_2$ per cent interest and amortization charge we have

Fixed charges	$15,482.00
Electrical energy at $0.004	23,770.00
	$39,252.00

This clearly illustrates the extravagance in the use of electrical energy for the oxidation of ammonia.

The arguments were brought forth by the electrically heated type of catalyst enthusiasts that the cost of electrical energy per ton of nitric acid was small, yet the commercial comparison of Table 3 showed the true merits of the case as applied to the oxidation of high grade coke oven ammonia. If we consider merely the cost of electrical energy and assume it can be purchased at $0.004 per k. w. h., then we have an electrical energy charge of $0.00071 per lb. of anhydrous nitric acid. This is a little more than twice the charge against platinum depreciation. It also is nearly 50 per cent of the total operating labor costs of a plant using multi-layer types of converters without external heat energy. In the light of such analogies the charge is an important one.

Assuming the market price of NH_3 is $0.10 per lb., it would be necessary to save 389,520 lbs. of NH_3 per year when using an electrically heated catalyst for the oxidation of coke oven ammonia. This means that it will be necessary to secure 3.5 per cent greater conversions by the use of an electrically heated type of converter than on a non-electrically heated type in order to have both types as close competitors.

The above calculations were not based upon the use of impure grades of coke oven ammonia, such as powder liquor, or upon cyanamide ammonia.

The availability of the added electrical equipment and the installation of such in urgent periods must also be a consideration in the ultimate decision of what type of catalyst to employ.

It was this situation which influenced the decision for the cylindrical converter at Plant No. 1. It should be borne in mind that the development work upon this problem was far from complete at the time when the war demands for an ammonia oxidation plant were pressing. The simplest equipment obtainable, and one which would produce the required material, was desired. The data secured for the Nitrate Division of the Ordnance Department by Lieut. C. F. Brush, Jr., Lieut. G. Cawley, and Mr. J. D. Davis, of the Bureau of Mines, during April and May 1918, certainly warranted the installation of such a type of converter.

For six months prior to the operations at U. S. Nitrate Plant No. 1, four members of the Nitrate Division of the Ordnance Department had been assigned to the study of the general plant details of the whole ammonia oxidation problem. The semi-commercial installations at the plant of the American Cyanamid Company and the plant of the Semet-Solvay Company served as experimental stations. The courtesies of the representatives of these two companies were thoroughly appreciated.

LIMITATIONS OF NON-HEATED FORM

It was during this period that certain limitations to the utilization of the non-electrically heated form of catalyst became most apparent.

While the initial work by the Bureau of Mines and the Nitrate Division had consisted in the general development of the thermal features of the catalyst, together with a general study of plant design, including absorption of oxides of nitrogen, it seemed now that other factors greatly influenced the oxidation efficiency.

The influence of an excess of oxygen, the importance of a pre-activation of the platinum surface, the catalytic decomposition of ammonia at fairly low temperatures, the space permissible between the separate gauze layers, the economical number of gauze layers, and the influence of gas velocity to catalyst surface had all only been touched at the high spots in the initial investigations.

CATALYST PURITY—The influence of various platinum group metals upon the platinum has been the source of considerable discussion. Dr. Landis' patent[1] is rather clear in expressing that the presence of traces of iridium is very objectionable. Even in the recent article by Dr. Landis[2] he reports "and it was noted that the presence of iridium had a particularly deleterious effect." Since other factors were seriously influencing the temperature functions of the catalyst it seemed wise to utilize the very highest grade of platinum that could be produced. Through the excellent coöperative spirit of the representatives of the U. S. Assay Office of New York City it was found possible to secure very high grade platinum for the gauzes to be used at U. S. Nitrate Plants Nos. 1 and 2.

TABLE 4

	A	B	C	D	E
Pt, per cent	98.67	99.14	99.02	99.41	99.95
Ir, per cent	0.28	0.027	0.21	0.07	..
Rh, per cent	1.08	0.50	0.34	0.27	..
Pd, per cent	0.12	...	0.004	Trace	..
Fe, per cent	0.32	0.236	0.16	0.06	
Mesh	80	100	80	80	80
Diam. wire, inches	0.0026	0.0026	0.0026	0.003	0.003
Results	Good	Bad	Bad	Fair	Good

The quality of the platinum in the finished gauze was of such high standard that but mere traces of impurities could be detected. The analyses of gauzes which were used in various commercial tests are given in Table 4. The A, B, C, and D analyses were conducted by the Bureau of Standards.

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[1] U. S. Patent 1,193,799.

[2] *Chem. & Met. Eng.*, **20** (1919), 472.

Gauze A was used over a long period and it performed as well as E. Excellent oxidation conversions resulted with A and E, while it appeared that gauze C gave distinctly poor efficiencies under apparently similar conditions. It was most difficult to distinguish the commercial oxidation efficiencies obtained from the A gauze as apart from those of the E gauzes of practically pure platinum. It should be noted that these comments apply strictly to the use of the above gauzes in the oxidation of a high grade of coke oven ammonia. The conclusions were that under similar plant operating conditions it had seemed most difficult to detect serious differences in the action of platinum gauzes containing small amounts of iridium from those of essentially iridium-free quality, when utilizing coke oven ammonia.

The experimental station connected with U. S. Nitrate Plant No. 1 was asked to check up carefully the above indications by a series of tests upon known alloys of platinum and iridium alone. The results were a verification for the above commercial observations.

The minor importance of the extreme chemical purity of the platinum and the major effect of catalyst temperature were rather well established.

In spite of the general increase of knowledge along these lines the fact that many inconsistencies and occasional drops in conversions were confronted made the problem worthy of more serious thought. Before continuing the investigation of these inconsistencies it had seemed wise to study the theoretical limitations. A very brief abstract of the considerations will serve to illustrate the points.

The first commercial operations of the Oxidation Unit at U. S. Nitrate Plant No. 1 were conducted on July 2, 1918. Grade B coke oven aqua had been secured as the source of ammonia for the initial testing of the plant. Although the plant was designed for the commercial oxidation of a pure synthetic ammonia, arrangements had been made to continue the development of the more important projects together with the actual production. The various demands of the first few months prevented very extensive investigations and the major portion of the work was involved in regular production problems.

REACTION VELOCITY—Low oxidation efficiencies must apparently be due either to the passage of unoxidized ammonia or else to its oxidation to nitrogen. It is probable that it is impossible to detect the quantity of NH_3 passing through a catalyst as such, since the temperature conditions between the catalyst and the point of sampling are sufficient to cause decomposition of the ammonia. At any rate, we may consider the typical probable cause of low conversions as due ultimately to

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O$$

or

$$\frac{(P_{N_2})^2 \quad (P_{H_2O})^6}{(P_{NH_3})^4 \ (P_{O_2})^3} = K_2 \qquad (12)$$

and we have previously seen that

$$\frac{(P_{NO})^4 \quad (P_{H_2O})^6}{(P_{NH_3})^4 \ (P_{O_2})^5} = K_1. \qquad (8)$$

The nitrogen formation reaction can doubtless be considered as a two-stage reaction, or bi-molecular, for

$$4NH_3 \longrightarrow 2N_2 + 6H_2 \qquad (13)$$

and

$$6H_2 + 3O_2 \longrightarrow 6H_2O \qquad (14)$$

but the NO formation reaction cannot be classified in such a simple order of reactions, since the temperature conditions of the reaction are far too low for the union of nitrogen and oxygen. There would probably be some hesitancy in considering the NO formation reaction as one of the ninth order, yet it is more complicated than the nitrogen formation reaction. Under these conditions of complexity of reaction one would expect to find a higher velocity for the NO reaction than for the N_2 reaction. At present it is difficult to identify the exact dynamics of this reaction.

Then, too, at from 650° C. to 1000° C. the velocity of the initial NH_3 decomposition is very low under ordinary conditions in the absence of a catalyst and it is quite difficult to see how the above reactions, 13 and 14, should occur unless these were also catalyzed by the platinum gauze. It seems most clear that we are dealing with the preferential catalysis of the direct oxidation reaction over that of the ammonia decomposition reaction. The study of the temperature, velocity, concentration, and poison functions were considered from this viewpoint. The definitions of the exact temperature, velocity and concentration conditions at which the NO formation reaction was maximum and the NH_3 decomposition reaction a minimum, with a platinum catalyst, were the conditions sought.

CONTACT AGENT—The contact surface required for the preferential oxidation reaction is absolutely dependent upon the temperature-reaction-velocity relationships. An excessively large contact surface and a low gas velocity at any temperature above 600° C. favor the ammonia decomposition reaction and the catalytic decomposition of NO to nitrogen and oxygen. The existence of these two important catalytic actions are the limiting conditions for the thickness of the catalyst material. It is true that a high gas velocity, at a high temperature, offers a method of correcting for excessively large contact surfaces. However, a high velocity at too low a temperature must permit the passage of unchanged ammonia.

Up to the present time the most ideal platinum catalyst is probably the one in form of a gauze or net. In view of the apparent ease in control of the catalyst surface it is an excellent form with which to secure comparative data. Although platinum gauze of 0.0020 in., 0.0026 in., and 0.003 in. diameter wires, from 80 to 100 mesh, has been used, it is interesting to consider a single layer of these gauzes from a theoretical viewpoint. The important features in the choice of a metallic wire catalyst are *active surface*, *gas space*, *mechanical strength*, and *weight*.

All things being equal, the active surface per unit surface area (1 sq. in.) per actual weight is the important limiting factor involved in an estimate of capacity. There will doubtless be a difference of opinion as to what constitutes the active surface of a platinum wire gauze. Observation of the action of many commercial gauzes has led the writer to believe that only approximately one-half of the cylindrical surface of the wires is to be considered as active when using a one-layer catalyst. A new platinum wire does not promote the oxidation reaction without the application of external heat energy. This so-called pre-activation of the new, smooth, platinum wire gauze may be accomplished by applying electrical energy to the gauze or else by placing the gauze approximately $^1/_{16}$ in. behind an active gauze of the same surface area.

Lieut. George Cawley began some work under the direction of the writer along a study of separated gauze layers. This work was interrupted for a time due to the demands upon Lieut. Cawley for other important work. It has since developed into a very interesting study of what constitutes the real catalytic reaction. The use of a separating heat conducting, coarse mesh gauze (Pt of $^1/_{16}$ in. wire and 4 mesh) between the activated front gauze and the non-active catalyst is exceedingly beneficial since it favors equality of heat distribution and presents the whole upper half surface of the platinum wires to the gas stream. When the newer layer is firmly attached to the old layer months are required for the activation of the new platinum, but with the proper spacing the activation is rapidly promoted. This has a great bearing upon the proper spacing of the layers of platinum in a multi-layer gauze. These more intricate features will be discussed in a separate paper. It is a simple matter to calculate the surface of the upper half of the cylindrical wires and in so doing it is desirable to deduct the area of the crossed wires. The data of Table 5 are based upon such calculations.[1]

The resistance offered to the gas flow is rather important in a proper design of a catalyst. An approximate measure of this is obtained by the knowledge of the gas space per total unit surface (1 sq. in.). The data of Table 5 refers to the free gas space not occupied by the wires of the catalyst. It is certain that the smaller this gas space the greater must the resistance to the passage of the gas become, and the smaller the number of gas molecules which can pass the gap without making contact with the wire surface.

The mechanical strength of a given platinum gauze becomes important when single layers are employed. A relative estimate would, offhand, be secured by a comparison of the combined area of the transverse wires per linear inch of gauze. Unfortunately, this estimate is subject to the activation phenomena. It is well known that a platinum wire develops a multiplicity of sprouts over its entire upper surface after it has been employed in the oxidation process for a period. The longer the term of service of a given wire the more elaborately sprouted it becomes. As a matter of fact, this feature is entirely the limiting factor in the choice of the proper diameter of wire to adopt for the catalyst. While it is possible to utilize wire diameters below 0.002 in., it is decidedly uneconomical due to the continued replacement costs. The cross section per linear inch is expressed in circular mils in Table 5.

The writer has a knowledge of certain semi-commercial experimental data which were secured in the choice of the most satisfactory diameter of wire for the platinum gauze. The size of the wire diameters was increased from 0.0015 in. while the mesh was maintained constant. It is quite evident that such experimental data are difficult to interpret unless the ratio of the gas space to active surface is maintained constant. With a constant mesh, an increase in the wire diameter certainly decreases the size of the openings between the wires, and thus two variables are being altered at the same time. The influence of the size of wire at a given mesh is shown by noting the fifth column of Table 5.

TABLE 5

Diam. Wire, In.	Mesh	Sq. In. Active Surface per Sq. In. Area	Wt. in Ozs. per Sq. In.	Sq. In. Gas Space per Sq. In. Area	Cross Section per Lin. In.
0.003	80	0.696	0.0150	0.578	720
0.0026	80	0.611	0.0108	0.628	540
0.002	80	0.477	0.0064	0.705	320
0.003	100	0.852	0.0181	0.490	900
0.0026	100	0.748	0.0136	0.549	676
0.002	100	0.588	0.0081	0.640	400
0.003	120	1.002	0.0216	0.410	1080
0.0026	120	0.884	0.0162	0.473	811
0.002	120	0.696	0.0096	0.578	480
0.003	150	1.212	0.0270	0.302	1350
0.0026	150	1.084	0.0206	0.370	1014
0.002	150	0.853	0.0120	0.488	600

An examination of the data clearly indicates the extra expense involved in the use of 0.003 in. diameter wire at 80 mesh over the wire gauzes of finer diameter. Although a rapid survey of the table shows that the 0.002 in. diameter wire at 120 mesh has the same active surface per unit area as the 0.003 in. diameter wire at 80 mesh and weighs but 64 per cent as much as the 0.003 in. gauze, yet from the standpoint of economy the writer believes that the use of a 0.0026 in. diameter Pt (Ir : 0.1 per cent) wire of 120 mesh is the desirable gauze material for a single-layer type of catalyst. When finer diameters and meshes are required the excessive fabrication costs, and replacements due to weakening by sprouting more than overweigh the saving in platinum which is created. Of course, the cost of platinum per ton of nitric acid is small for small installations so that this feature has the more important commercial significance when there is a scarcity of platinum. We can consider that under ideal conditions the plain 4-layer gauze with 0.0026 in. diameter wire and 80 mesh will commercially oxidize nearly 70 lbs. of Grade A NH_3 per oz. of platinum per day. It seems quite probable that the average life of the platinum under continuous 24-hr. service will be in the order of 275 days. One ounce of fabricated platinum gauze has a present-day value of approximately $115 and, of this, the base value of the platinum is in the order of $100. During these 275 days there will be an approximate loss of 0.05

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[1] A. A. Campbell, THIS JOURNAL, 11 (1919), 468.

ounce of platinum per ounce (*i. e.*, 5 per cent) due to dusting of the sprouts. There is also a fabrication loss of about 0.004 ounce per ounce. The total decrease in value of the platinum per ounce in 275 days is approximately $20.40. During this period this material will have oxidized 19,250 lbs. of NH_3, or will have produced 65,450 lbs. of HNO_3 (100 per cent). Therefore, each pound of nitric acid produced is made at a platinum expense of $0.0003 per lb. of anhydrous nitric acid. However, this means that the daily platinum loss for a 30,000 lbs. NH_3 per day oxidation unit amounts to $306 and, of course, this feature should be considered on large plant installations, since this is approximately equal to one-fourth of the total operating expense.

USE OF MULTI-LAYER GAUZE

The use of multi-layer gauze as a catalyst involves many interesting features. It is absolutely certain that the specifications for the inner, or first, layer of gauze should be quite different from those of the second, and so on.

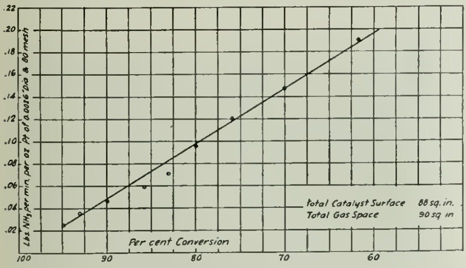

Fig. 1

An enormous amount of data has been secured upon the use of a multi-layer gauze. The first utilization of more than one layer was developed from efforts to decrease first installation costs, as well as to eliminate excessive heat losses. The economical upper limit to the size is not governed wholly by the limitation as to size of apparatus. Provided the catalyst chamber is so designed as to adjust carefully the rate of gas flow and temperature to the available contact surface, it is difficult to predict the upper limit to the size of a catalyst chamber. It is true that the control on the distribution of the intake gases to the catalyst might become somewhat complex when dealing with a converter which was the size of a blast furnace. There is, however, an economical upper limit to the number of gauze layers which should be employed when oxidizing ammonia-air mixtures. The data as plotted in the curve of Fig. 1 approximate the average data secured by many independent analysts upon the use of a single layer of catalyst at approximately a given set of temperature and contact surface conditions. The data apply to the use of Grade A coke oven aqua ammonia or its equivalent. The data as illustrated by the curve of Fig. 1 may be subject to some errors due to small changes in temperature, velocity, and contact time. All of the early information and data upon the capacities of various types of catalysts involved the serious variation of two independent variables: the weight of NH_3 oxidized per unit time, and the time of contact. The usual procedure, in a commercial or semi-commercial study, has been to increase the weight of NH_3 by increasing the total ammonia-air gas flow per total gauze surface (gas space + wire space) with a fixed volume percentage of NH_3. Attempts to control the weight percentage of NH_3 for a fixed contact time involved the necessity of altering the ratio of nitrogen and oxygen to the ammonia in the intake mixture. Otherwise, the third independent factor, the oxygen concentration, became variable. While the above procedure gave the data for commercial application to the use of air as the source of the oxygen, nevertheless the majority of data is scientifically quite inaccurate. An interesting study involves the use of separate supplies of nitrogen, oxygen, and ammonia. The ratio of oxygen to ammonia can be maintained constant, and yet the variation of conversion with time of contact at constant capacity, or the capacity at constant time of contact, can be secured. These data become important when spillage oxygen is available. The studies along this line will be published at a later date.

It is rather easy to approximate the time of contact when using a single layer of gauze. Rather good commercial yields are obtained when a single electrically heated gauze at about 800 to 850° C. is oxidizing 20 cu. ft. per min. of a 10 per cent (by vol.) NH_3-air mixture per sq. ft. of total gauze surface. This corresponds to 0.086 lb. NH_3 per 1.56 oz. on 1 sq. ft. of total gauze surface. Since this rate applies to the use of an 0.0026 in., 80-mesh wire gauze, we have

$$\text{Average contact time} = \frac{\text{Free gas space area} \times \text{wire diameter}}{\text{Cu. ft. gas flow per second}}$$

or,

$$\frac{0.628 \times \dfrac{0.0026}{12}}{20 \times 60} = 0.0011 \text{ second.}$$

The calculation of the time of contact for a multilayer close contact gauze must make serious assumptions and, at the best, the final deduction is a guess. We do know that the time of gas contact within the first layer is very much less than in the case of a single layer.

For temperatures approximating 850° C., as maintained by electrical heating, the data are at least comparable for actual commercial operations. The feature of the illustration is to point out the enormous percentage of work carried out by the first layer of catalyst.

It is very important to remember the above approximations. The normal capacity of a platinum electrically heated gauze for commercial practice is in the order of 0.055 lb. of NH_3 per oz. of platinum per min. when using an 0.0026 in. diameter and 80-mesh gauze, and giving 90 to 91 per cent conversion on Grade A ammonia. (When using an 0.003 in.

diameter wire and 80 mesh the yield drops to approximately 0.032 lb. NH_3 per min.) When increasing the work placed upon a unit surface of catalyst per unit time to nearly fivefold, there is only an efficiency drop of about 33 per cent. Of course, the important feature is the distribution of this 33 per cent between loss due to the ammonia passing the catalyst as such, and ammonia which is decomposed to nitrogen. Unfortunately, when an attempt is made to test for NH_3 in the presence of the exit mixture which is being passed at a high rate, it is most difficult to account for much. It is quite evident that during the period between the time of taking the sample and the analytical determination there is an interaction of the NH_3 in the presence of NO, O_2, and H_2O, with the resultant decomposition of the NH_3.

When using four layers of superimposed gauze it has been the commercial practice in the United States to mount these layers in close contact. Under such conditions it was found that approximately four times the normal quantity of NH_3 could be delivered to the upper layer; yet, as applied to the total weight of platinum (4 layers) involved, an approximate yield of the same 0.055 lb. of NH_3 per oz. of platinum per min. was obtained. This would be rather good evidence of the fact that the large share of the NH_3 which passes the first layer of gauze at high gas velocities does so without decomposition within the first layer of catalyst. When using four layers of catalyst which are in intimate contact it has been observed that the oxidation efficiency begins to decrease with the passage of more than 0.055 lb. of NH_3 per oz. of platinum per min. Under these conditions the first layer is subjected to four times its normal rated capacity of NH_3 in a much shorter contact time. From the tests upon the single layer it might be assumed that this first layer was doing about 70 per cent of the total work of the whole four layers. Any effort to increase the working capacity of the second, third and fourth layers by merely increasing the weight of ammonia delivered in unit time results in a drop in the conversion. However, such an effort has usually involved variations in the oxygen, ammonia or temperature variables. These facts are rather a good argument for the use of different mesh gauzes in the various layers and the separation of such. If the first layer must be operated so as to accomplish 60 to 70 per cent of the total oxidation, then the contact surface-gas ratio (*i. e.*, ratio of wire diameter to mesh) should be quite different for the first layer, handling a 10 per cent NH_3 mixture, than for the second, handling a more dilute gas mixture and possibly at a slightly higher temperature.

When using a multi-layer platinum gauze catalyst, in which the layers are in intimate contact, it would seem as if the layer percentage oxidation secured by any number of layers greater than three is exceedingly small. The decision as to the use of more than three layers of gauze must rest upon a comparison of the costs of each additional layer of platinum gauze and its depreciation charges to the cost of one new converter casing and fittings. In the absence of electrical heating, or a heat interchanger, it is considered by some authorities that each additional gauze layer functions by producing a higher catalyst temperature. It is exceedingly doubtful whether the decrease in radiation and conduction losses by the use of each layer above three can possibly overweigh the extravagant use of these extra layers. It is true that the use of each succeeding layer after the first results in a smaller combined heat loss than if the extra layers of gauze were installed in multiple units, but there are much more efficient methods available for this heat conservation. A quantitative statement of these heat losses for varying numbers of layers of catalyst cannot be made. Such commercial data are exceedingly difficult to secure. Then, too, the loss in actual exposed platinum surface, by the intimate contact of the under surface of the upper layer with the upper surface of the succeeding layer, is of a high percentage magnitude. While the original intent in the use of a multilayer gauze consisted in efforts to increase thermal capacity, this should not be accomplished at an extravagant expense of platinum. It is true that there is an approximate platinum loss amounting to about \$0.00031 per lb. of anhydrous nitric acid produced (based on the price of \$115 per oz. of fabricated gauze), and if we assume an NH_3 basic price of \$0.10 per lb. it is easy to find that an increase in oxidation efficiency of one per cent decreases the cost of nitric acid (100 per cent) \$0.0003 per lb. The relative importance of increasing the efficiency by one per cent with the possible use of added layers of gauze as compared to the increased platinum thus utilized is very apparent.

It is a difficult matter actually to grasp the real situation involved in the use of a single layer of gauze. In the case of a 0.003 in. diameter wire and 80-mesh gauze there is actually a free gas space of 57.8 per cent of the total exposed space. If it is desired to prevent loss of ammonia molecules through failure to come in contact with the platinum surface, the logical procedure is to decrease these free gas spaces by means of an increased mesh and a second or third layer of catalyst. The idea of catalysis within the gas zone itself has been suggested but the idea is rather vague. Assuming that the reaction is one of catalysis, and that the catalytic agent is the multiplicity of platinum sprouts on the gauze surfaces, then the first important step in catalyst design is an effort to secure the maximum gas contact with the smallest amount of platinum. Certainly a single layer of a gauze with 57 per cent free gas space cannot give the best results. This viewpoint has led some investigators to adopt the use of various carriers as the embedding medium for platinum sponge. Due to the ease of decomposition of the ammonia such porous carriers as alundum, etc., have caused all sorts of troubles. Filtros plates have been used with but fair success. Thin film deposits, as well as various platinum clad metallic wires, have been suggested, but due to the continued sprouting of the platinum during the oxidation reaction it appears that the mechanical disintegration must become serious within a short time.

The limitations of thin platinum films or wires have been clearly demonstrated at U. S. Nitrate Plant No. 1. For a long period it was considered advisable to have very intimate contact of the different gauze layers in a multi-layer type of converter. These layers were welded together by means of a small pointed hammer, maintaining the gauze at a dull red heat at the point of welding. This method was also applicable to the repair of gauzes which had been injured. At the point where the welding of the gauze had been obtained the wires were necessarily flattened to a very thin strip. It has been observed that these points fall to shreds after two or three months of service. This is well illustrated in the photograph of a used 4-layer spot welded gauze in Fig. 2. Microscopic examination has shown that the thin layers have become sprouted through the complete width of the wire. The sprouts have but little strength and at such points upon the gauze there is crumbling and a complete loss of the platinum. It is true that a thin film in the presence of a suitable carrier would not exhibit this behavior, yet the choice of a carrier is most limited.

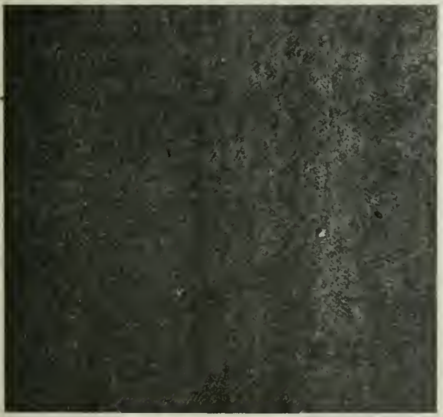

Fig. 2

The use of the smallest possible spacings between the wires, the smallest diameter consistent with rigidity after the platinum has developed sprouts, and more than one layer of gauze, would seem to be the first logical requirements for a platinum wire gauze catalyst. Some interesting calculations are obtained when studying the relationships of the mean free path of the molecules involved in the reaction of the gas space of various diameters and meshes of gauze.

It is certain that an expression of the time of contact of the gas with the contact surface has little meaning without the statement of the temperature for that time of contact. Whether nitrogen or nitric oxide is formed under a specific period of contact depends greatly upon the temperature, which in turn governs the relative reaction velocities of the two above-mentioned reactions when in the presence of platinum.

OXYGEN CONCENTRATION—A consideration of Reactions 8 and 12 in reference to the influence of oxygen upon the reactions is interesting. By application of the law of mass action we can predict what variations will occur within the system with change in concentration, as well as the velocity with which the equilibrium is attained. The velocity of the NO Reaction 8 is proportional to the fifth power of the oxygen concentration, while that of the decomposition Reaction 12 is proportional only to the third power of the oxygen concentration. It is evident that it would be desirable to secure the highest oxygen concentration possible in order to favor the NO formation reaction. This method of procedure is not commercially practicable in all instances. In the case of the production of nitrogen from the liquefaction of air, for use in either the cyanamide process or for the synthetic production of ammonia, it is certain that there is established an excellent source of oxygen for assisting the preferential oxidation of the ammonia to NO.

Another function of an excess of oxygen has been involved in the elimination of certain poisonous constituents such as excessive pyridine, naphthalene, etc., in coke oven ammonia gas mixtures. In case there are even only small percentages of these substances present it is evident that in the case of a molecule like naphthalene there is a large oxygen requirement when it is oxidized. This reaction occurs at the temperature and conditions of the ammonia oxidation catalyst. The excess of oxygen, when using high NH_3 mixtures, can thereby be decreased to such an extent that the ammonia decomposition reaction (nitrogen formation) is greatly favored. This type of catalyst poisoning has been encountered in the oxidation of poorer grades of coke oven ammonia, such as the so-called "B" and "powder" grades of ammonia liquors. The function of the constituents of the gas mixture to be oxidized is very important in certain instances. The problem is simple when applied to the oxidation of synthetic ammonia, but is much more complicated when considering coke oven or cyanamide ammonia. An illustration of these effects will be discussed in a later paragraph.

A study of the two previously mentioned reactions shows that any increase in the nitrogen concentrations of the ammonia mixture will tend to force back the decomposition reaction (nitrogen equilibrium). Thus the nitrogen of the air can serve the purpose of decreasing the ammonia decomposition reaction. It is apparent that the ideal ammonia oxidation system should involve the use of the exit gases from the NO_2 absorption system as well as the utilization of the oxygen from the liquid air unit, if such a system of nitrogen production is employed near the plant. The gases which leave the ammonia oxidation absorption system are very rich in nitrogen and by a proper proportion of these gases with by-product oxygen, the most satisfactory concentration of nitrogen and oxygen can be obtained. An oxygen concentration 25 per cent greater than that demanded by the NO formation reaction is desirable for the best results.

It is impossible to secure this by the use of air as the source of oxygen.

The theoretical NH_3 concentration demanded by the reaction

$$4NH_3 + 5O_2 + 18.8N_2 + Pt = 4NO + 18.8N_2 + 6H_2O + Pt \quad (15)$$

is 14.4 per cent, yet, when using saturated air as the source of oxygen, it will be observed that the ideal oxygen requirements are not fulfilled on a 14.4 per cent NH_3. The decreased oxygen content then merely favors the nitrogen formation reaction and greatly decreased oxidation efficiencies occur under these conditions, particularly in large plant operations. Of course, a process for selectively abstracting the undesirable excess of nitrogen in a 14.4 per cent NH_3-air mixture would solve the problem.

PRESSURE INFLUENCE—The change of volume as indicated by Reaction 15 is exceedingly small. Whether pressure has any great selective influence upon the above two reactions as carried out in a commercial manner is problematical. Since at ordinary atmospheric conditions it has been previously indicated that the theoretical equilibrium called for a conversion of NH_3 to NO at above 99 per cent with all temperatures up to 1200° C., it did not seem worth while to worry a great deal over the pressure factor as a means of increasing the conversion efficiencies. The influence of this factor upon the capacity opens a possible source of investigation, yet other factors seemed to be of greater importance for the initial studies.

(*To be concluded in our next issue*)

A CONTINUOUS PROCESS FOR ELECTROLYTIC REGENERATION OF CHROMIC ACID[1]

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Received July 8, 1919

The problem of developing a continuous process for electrolytic regeneration of chromic acid from waste liquor is one of considerable commercial importance.

Chromic acid is one of the most important oxidizing agents used in chemical processes for the oxidation of organic compounds. During oxidation the chromic acid in the solution is reduced to chromium sulfate, which usually goes to the sewer. To recover the chromic acid from this waste liquor by a chemical process is not advisable, not only for commercial reasons but also on account of the difficulties and complications involved in such processes. Hence a process of electrolytic regeneration of the chromium solution, if completely worked out to the point of commercial application, would be not only a matter of scientific interest but a real contribution to industrial development. As an illustration, factories employ chromic acid solution for oxidation of organic compounds in the manufacture of camphor, organic acids, etc. At present, in one New Jersey plant, this spent liquor with about 10 per cent chromium oxide, amounting to about 200,000 lbs. per month, is run to waste. If the process for electrolytic regeneration of this waste liquor can be worked out to commercial advantage, it means that not only the trouble of disposing of acid and troublesome waste liquor and of preparing fresh chromic acid solution will be avoided, but the cost of sodium bichromate and sulfuric acid will be replaced by a relatively insignificant expense for electric current.

LITERATURE

The electrolytic regeneration of chromic acid was first attempted by Fitzgerald in 1886,[1] using acid chromic salt solution as the anode liquor and zinc sulfate as the cathode liquor. The process was not practical because of the loss of zinc sulfate.

In 1893, Dr. Karl Haussermann[2] described a process in which he prepared chromate from sodium chromite by electrolytic oxidation in alkaline solution and then transformed the chromate into bichromate.

In 1899, Dr. F. Regelsberger[3] did some work along the line of electrolytic oxidation of a chromic salt solution. It comprised: (1) oxidation in the alkaline solution using chromic hydroxide, and (2) oxidation of chromic salt in acid solution. In the latter case the cathode employed was either lead, iron, nickel, or copper, the anode being lead.

Later, Dr. Karl Elbs[4] in his manual gave a summary of the process of oxidizing chrome alum in acid solutions.

According to Dr. Regelsberger,[5] it is the lead dioxide formed on the surface of the lead anode that really acts as the agent for the oxidation of chromic salt to chromic acid.

In this connection Muller and Soller[6] made an investigation in 1905 concerning the behavior of a lead dioxide anode and showed it to act catalytically as in the oxidation of iodic acid into periodic acid.

Before this time, in 1898, Meister Lucius and Brüning[7] had taken out two patents, one in Germany and the other in Great Britain, in which a cyclic process for sulfuric acid concentration in connection with the electrolytic regeneration of chromic solution was devised. The process is to place the chromic acid solution in the cathode section in place of pure sulfuric acid and then to pass an electric current long enough to oxidize the corresponding liquid in the anode section. The anode liquor is to be used directly in the works whereby chromium oxide is again formed and is then allowed to flow into the cathode section when it is again to be electrolyzed. The solution used in the previous run in the cathode section is now used in the anode section. Before the second electrolysis the cathode solution is richer in sulfuric acid than the anode solution but this time the excess migrates to the latter solution. A cyclic process is thus carried out in which the chromic acid solution is alternately placed in the anode and cathode chambers, thus preventing the accumulation of an excess of sulfuric acid in it and making it possible to maintain the solution at a given concentration during its regeneration by electrolysis.

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[1] Submitted by Shoo Tze Leo in partial fulfillment of the requirement for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, New York City.

[1] Brit. Patent 5,542 (1886).

[2] *Z. angew. Chem.*, **1893**, 363; and Wickop, "Die Herstellung der Alkali Bichromate," **1911**.

[3] *Z. angew. Chem.*, **1899**, 1123.

[4] "Elektrolytische Darstellung chemische Präparate," **1902**.

[5] *Z. Elektrochem.*, **6**, 308.

[6] *Ibid.*, **11**, 863.

[7] *Ibid.*, **6**, 256; O. Imray, *J. Soc. Chem. Ind.*, **18**, 685; D. R. P. 103,860, June 12, 1898; Brit. Patent, 15,724, July 18, 1898; cf. also Le Blanc, *Electrochem.*

In 1899, Darmstadter[1] developed a process in which he tried to regulate the current density in such a manner as to make the migration of sulfate ion equal to the diffusion rate, so that the sulfuric acid concentration would be balanced. In the same year Darmstadter[2] secured another German patent in which he stated that the current was to be stopped for a time to let the diffusion of the solution go on as referred to in the previous patent.

In regard to the electrolytic oxidation in alkaline solution, the Chemische Fabrik Griesheim-Electron[3] worked out a process in 1901 by using a mixture of chromium sulfate and sodium sulfate solutions which was kept alkaline. A soluble anode such as chromium or ferrochromium was used.

The same firm[4] developed in the same year another process which was the same as the above, except that an insoluble anode was used instead of a soluble anode.

Le Blanc[5] discussed this subject at length and laid special emphasis on the question of diaphragm. One of the methods he used to prepare an acid-resistant diaphragm was to make plates which are rather plastic before heating by using a mixture of 25 per cent alumina and 75 per cent silica. The chief difficulty in preparing such a porous diaphragm lies in combining good conductivity with good mechanical strength.

In 1913, Paul Askenasy and A. Revai[6] tried to develop a technical process of chromic acid regeneration without the use of a diaphragm. They conducted their experiments by using high cathode current densities, by adding magnesium sulfate, chromium sulfate, potassium sulfate, sodium sulfate, etc.

Earlier, in 1905, Le Blanc[7] developed another process which dispensed with the use of diaphragms by employing vessels in which the cathode and anode chambers were separated by partitions which did not extend entirely to the bottom of the vessel. The chromic salt solution was introduced at such a rate as to insure the requisite quantity of acid in the cathode chamber for the quiet progress of electrolysis. The current density was regulated so that the fresh addition of chromic salt solution would be first acted upon by the denser current.

Still another process which dispensed with the use of a diaphragm was developed by the Chemische Fabrik Buckau[8] in 1906, by which alkali sulfate or acetate or a mixture of both was added to the electrolyte so that the cathode potential was reduced to such extent that the reduction of the chromic acid by hydrogen formed at the cathode was avoided.

Schmiedt[1] made a special study in 1909 concerning the addition of various agents. Some of his work is of technical use. He found, for example:

Addition		Current Efficiency	
	Per cent	At Start Per cent	At Finish Per cent
No addition	...	82.2	71.3
KF	1.0	93.4	86.2
KF	0.1	92.8	73.9
Na_2HPO_4	1.0	98.2	82.8

Small quantities of boric acid, potassium cyanide and sodium vanadate and molybdate also had marked effect. The mechanism of these actions is not understood.

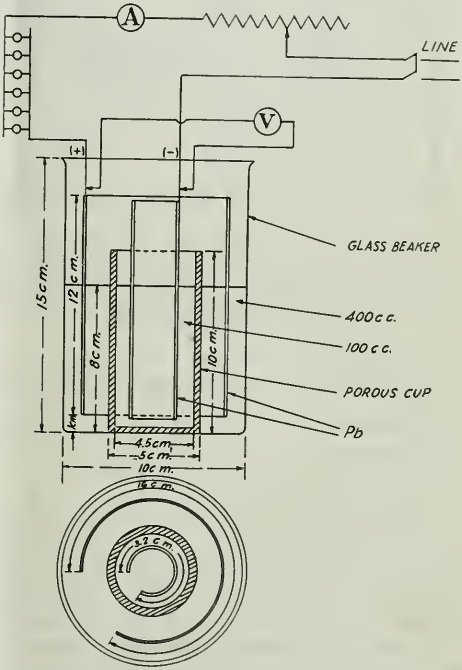

Fig. 1—Discontinuous Cell for Electrolytic Regeneration of Chromic Acid from Waste

Although there is considerable literature on the subject of electrolytic regeneration of chromic acid solution, it is apparent that this problem is far from being completely solved. First, no special emphasis has been laid upon the nature and quantity, if any, of the particular organic materials present in the chromium waste to be oxidized, a condition on which the success or failure of the process is likely to depend. Second, the information given lacks the essential details to insure a complete success of technical operation. Third, all the processes described in the literature are discontinuous, which means high labor cost and inconvenience in handling, consequently rendering the

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[1] D. R. P. 117,949, Nov. 3, 1899.

[2] D. R. P 138,411, June 8, 1900.

[3] D. R. P. 143,320, Feb. 8, 1901.

[4] D. R. P. 146,491, March 26, 1901.

[5] *Z. Elektrochem.*, **7**, 290.

[6] *Ibid.*, **19**, 344–62.

[7] D. R. P. 182,287, March 14, 1905; French Patent 362,195, Jan. 5, 1906; U. S. Patent 883,651, March 31, 1908.

[8] D. R. P. 199,248, May 9, 1906; Brit. Patent 9,636, April 25, 1907; U. S. Patent 895,930, Aug. 11, 1908.

[1] Dissertation, Charlottenburg, 1909; Allmand, Applied Electrochemistry.

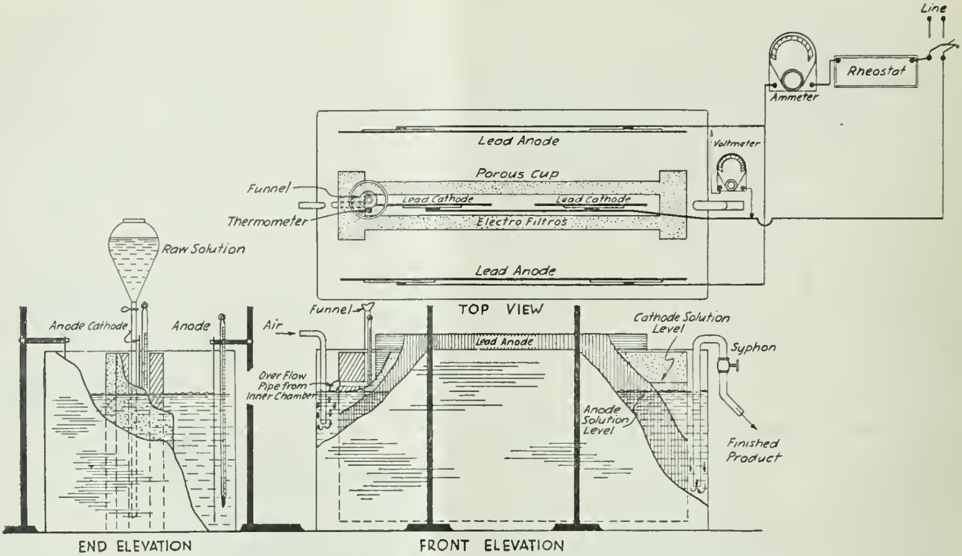


Fig. 2—Continuous Cell for Electrolytic Regeneration of Chromic Acid from Waste

process prohibitive economically for commercial applications. It is apparent that detailed experiments overcoming these difficulties must be made before the process is ready for commercial use.

EXPERIMENTAL WORK

The present investigation divided itself into three parts:

I—Elimination of organic matter and possibility of regeneration.

II—Determination of conditions in detail.

III—Continuous operation.

GENERAL PLAN—Before each of the steps (as outlined above) is taken up in detail, it is desirable to describe here the general plan which was followed in the early experiments. The discontinuous cell as shown in Fig. 1 consisted of a glass cylindrical jar with either an asbestos or porous clay cup placed in the center as a diaphragm. The anode of cylindrical shape was placed outside the cup, while the cathode was a narrow plate inside. These electrodes were made of lead. Their sizes varied for different experiments. The electrolyte consisted of the waste liquor with or without addition of sulfuric acid. In each experiment the waste liquor was first filtered through a sand bath about 2 in. deep to remove any suspended organic matter.

TESTING SAMPLES—During each experiment samples were taken from time to time to ascertain the acidity of the solution and the progress of oxidation. The acidity was determined by titrating against 0.5 *N* NaOH with phenolphthalein as indicator and the acid present calculated as sulfuric acid in grams per liter. The amount of chromium oxidized was determined by the iodine method. Ten cc. of 10 per cent KI solution were taken, 5 cc. conc. HCl added, and the sample to be tested run in. The iodine liberated was titrated against standard 0.2 *N* sodium thiosulfate solution and the amount of chromium oxidized calculated.

I—ELIMINATION OF ORGANIC MATTER AND POSSIBILITY OF REGENERATION

We start out in the solution of our problem with a qualitative determination of the possibility of the process. It involves two steps: (*a*) Elimination of organic matter; and (*b*) possibility of regeneration.

(*a*) ELIMINATION OF ORGANIC MATTER—The first step towards working out a continuous process for electrolytic regeneration of chromium from waste liquor is to destroy whatever organic matter may be present in the solution. As has been said before, the waste liquor at hand came directly from a factory in New Jersey. It contained about 230 g. sulfuric acid per liter and chromium sulfate to an extent of about 90 g. chromium oxide equivalent per liter. There was also present organic matter left over from the process of oxidation. This organic matter is objectionable and the quantity of it such that it gave a strong odor and an oily appearance to the waste. So long as the organic matter is present the process of regeneration by oxidation will be always subjected to reversal condition, *i. e.*, chromic acid will be reduced by the organic matter present. It was suggested that a steam distillation of the waste liquor or an extraction by a mineral oil might largely remove the organic matter. Tests showed that neither of these was effective. Apparently the method of simply using the current is the best, if the organic matter can be destroyed by it and not too much electric energy consumed in the process. This gives also, perhaps, the distinct advantage of labor and equipment economy in that it is only a single process instead of several processes.

A series of experiments using the current to remove the organic matter by oxidation, was conducted under conditions in which the current densities, sulfuric acid concentration, etc., varied. These experiments showed that it is quite possible to destroy the organic matter in such waste chromium liquor simply by the action of the current.

(*b*) POSSIBILITY OF REGENERATION—The next experiment was the qualitative determination of the possibility of regeneration, *i. e.*, to what extent the waste liquor can be recovered in the oxidized form at a reasonable expenditure of electric energy. In other words, approximately at what energy consumption, to what concentration of chromic anhydride in grams per liter, and with what per cent conversion of the chromium into chromic acid can this waste liquor be regenerated by electrolysis.

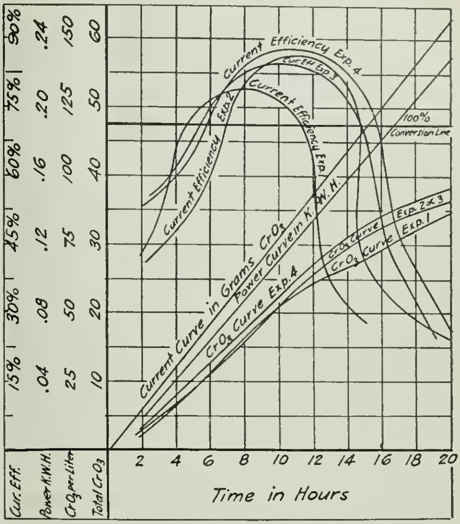
A series of experiments proved it possible to regenerate the chromic acid from this waste to an extent of at least 65 per cent conversion at a total current efficiency of about 35 to 40 per cent and at an energy consumption of 110 to 140 g. chromic anhydride per k. w. h. One thing which must be noted here, however, is that the experiments should by no means be interrupted, as at the points of each interruption there were always sharp decreases of current efficiency and increases in energy consumption.

II—DETERMINATION OF CONDITIONS IN DETAIL

(A) EFFECT OF MECHANICAL STIRRING—We know that oxidation, if possible, commences in every case when the anode potential has been raised above the equilibrium value for the given system. But in practice the polarization effects will occur to a greater or less extent, depending upon the fact that the ion capable of combining with oxygen may be exhausted and the oxidized ion may be accumulated in the immediate neighborhood of the anode. For this reason, mechanical stirring may be used advantageously to remove or reduce the concentration polarization by preventing the accumulation of $Cr_2O_7^=$ ion around the anode.

Air stirring may have some oxidizing effect, hence may be preferred to any mechanical stirring device.

In four experiments, as shown in Curve 1, a comparison of the results of Expt. 1 with those of Expt. 2, and the results of Expt. 3 with those of Expt. 4, shows plainly that the air stirring helps the process of oxidation though only to a small extent.



CURVE I—MECHANICAL STIRRING CURVE

(B) SULFURIC ACID CONCENTRATION OF THE ELECTROLYTE—Sulfuric acid is highly ionized and consequently renders the electrolyte very conductive. In Expts. 1 and 2, both the anolyte and catholyte consisted of the original waste liquor; in Expts. 3 and 4, the anolyte was the original waste liquor, but the catholyte contained 20 cc. concentrated sulfuric acid to every 80 cc. waste liquor. In the following experiments the solutions, unless otherwise specified, were similar to those in Expts. 3 and 4. The sulfuric acid was added to maintain the acid condition in the catholyte and so prevent the precipitation of chromium hydroxide after the experiment had been in operation for some time (as was the case in Expts. 1 and 2). In Expts. 3 and 4, the sulfuric acid concentration amounted to about 100 g. per liter at the end of the experiment. Consequently, the results in Expts. 3 and 4 are comparatively better than those in Expts. 1 and 2, as is shown by the following data:

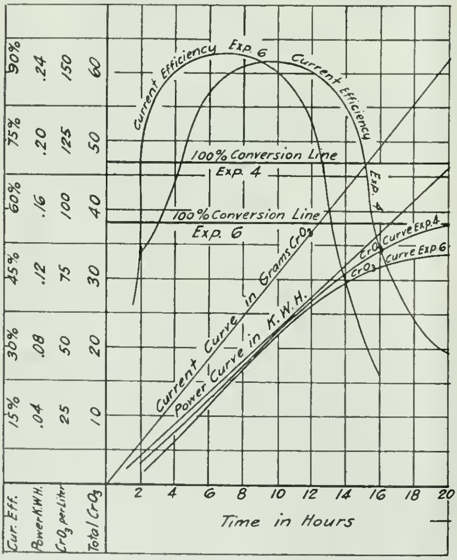
EXPERIMENT	Conversion Per cent	Total Current Efficiency	Grams CrO_3 per k. w. h.
1	78.4	54.1	150
2	75.5	57.2	155
3	76.9	58.3	188
4	77.6	65.2	221

To determine quantitatively the effect of sulfuric acid concentration Expts. 6 and 4 were compared, as shown in Curve 2.

To the point of 80 per cent conversion, Expt. 4 (without sulfuric acid) gives a total current efficiency of only 61.3 per cent with energy consumption of 206 g. chromic anhydride per k. w. h.; Expt. 6 (with sulfuric acid) gives a current efficiency of 70 per cent with energy consumption of about 240 g chromic anhydride per k. w. h. Thus the addition of sulfuric acid seems to produce better results so far as the per cent conversion is concerned.

On the other hand, a consideration of chromic anhydride content in the solution will throw a different light on the subject. With a chromic anhydride content of about 77 g. per liter, both Expts. 4 and 6 give about the same results, *i. e.*, total current efficiency about 70 per cent, energy consumption about 240 g. chromic anhydride per k. w. h. It means that if we consider the chromic anhydride content there is no difference with or without sulfuric acid. Besides, as shown in Curve 2, the current efficiency will be even higher and the energy consumption lower in Expt. 4 than in Expt. 6, if a further concentration of chromic anhydride in the solution is desired. Moreover, the addition of sulfuric acid would complicate factory operation.

(c) CONCENTRATION OF CHROMIC SALTS IN THE ELECTROLYTE—A process of electrolytic regeneration of chromic acid may be conceived as consisting of two simultaneous processes, (*a*) discharging of oxygen ion to form elementary oxygen, and (*b*) oxidation of the depolarizer, Cr^{+++}, by the elementary oxygen, to $Cr_2O_7^{=}$. The depolarization of the discharged oxygen ion by Cr^{+++} prevents the oxygen concentration from reaching the value necessary for gas evolution against atmospheric pressure. To the low concentration of oxygen corresponds a low electrolytic solution pressure, and the anodic potential needed for the process is consequently less than would be required for the discharge of gaseous oxygen. It is then evident that the velocity of the whole process depends essentially on the velocity of the second process. If this can keep pace with the velocity of the first process, the reaction will proceed with great current efficiency. But if the depolarization by chromium ion is slow, then the concentration of oxygen at the anode rises, its electrolytic solution pressure increases and the anodic potential necessary for the reaction becomes greater.



CURVE 2—H_2SO_4 CONCENTRATION CURVE

When the potential for oxygen discharge is reached, and part of the current produces oxygen gas instead of oxidizing chromium ions, not only will the voltage necessary for oxidation be increased, but the current efficiency will fall. The velocity of depolarization is therefore of great importance in electrolytic oxidation.

Hence, it is quite obvious that increase in concentration of depolarizer, chromium ion, will serve two purposes, (*a*) to keep down the anodic potential, and (*b*) to oppose concentration polarization to bring about more efficient depolarization, and to reduce current losses. Thus it may seem worth while to increase the chromic salt content in the regeneration of the waste.

A careful consideration will indicate, however, that such an increase by means of concentration is undesirable. It must be realized that concentration of chromic salt by evaporation, when the sulfuric acid content is about 230 g. per liter, is rather inadvisable, both because of the difficulty in handling and the high cost in operation.

Another way of changing the concentration of the chromic salt is to dilute the waste to a certain extent. From what has been said, such procedure will no doubt tend to make the results less favorable in so far as the question of depolarization is concerned. Furthermore, if the change of sulfuric acid is considered carefully, it is apparent that a dilution of the waste will decrease not only the chromic salt content, but also the sulfuric acid strength. It means that it will give not only a low concentration of chromic acid in the finished solution, but also a low current efficiency and high energy consumption for a definite amount of conversion.

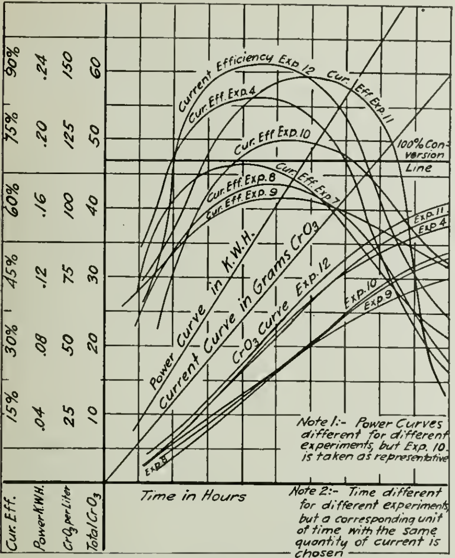
For all these reasons it is concluded that the change of chromic salt content in the waste either by evaporation or by dilution is not feasible.

(D) CURRENT DENSITY AT THE ANODE—An increase in current density will at least bring about two things, (*a*) an increase in anodic polarization and (*b*) a rise in anodic potential. With a high current density, not only more oxygen ions are discharged in a given time but also the layer of depolarizer around the anode becomes rapidly depleted. Both may cause an increase in the concentration of oxygen gas at the anode and in consequence there will be greater current losses. High current density invariably increases the overvoltage of oxygen. Therefore, in case the substance is very difficult to oxidize, it would be advisable to use high current density because it will raise the overvoltage.

Under these conditions, an increase in current density will tend to bring the potential of oxidation and that of free oxygen discharge further apart by raising the overvoltage of oxygen, thus remedying the situation. Hence, the effects of the change of current density may act favorably or otherwise according to the conditions.

Experiments (4, 7, 8, 9, 10, 11 and 12) with a current density of 2, 3, 4, 7, 9, 1, and 0.5 amperes per square decimeter, respectively, have been carried out for the purpose of studying the effect of current density (Curve 3). Comparison shows that Expts. 4, 11, and 12 with a current density of 2, 1, and 0.5 amperes per square decimeter, respectively, give better results than the rest, and the last experiment (Expt. 12) is the best. It gives 77 per cent conversion at a concentration of 91 g. chromic anhydride per liter, a total current efficiency of 72 per cent and an energy consumption of 276 g. chromic anhydride per k. w. h.

(E) TEMPERATURE—An increase in temperature will (*a*) increase the conductivity of the electrolyte and consequently reduce energy consumption, (*b*) increase the velocity of diffusion of the depolarizer, and (*c*) lower the overvoltage of oxygen and thus facilitate



Note 1:- Power Curves different for different experiments, but Exp. 10 is taken as representative

Note 2:- Time different for different experiments but a corresponding unit of time with the same quantity of current is chosen

CURVE 3—CURRENT DENSITY CURVE

the discharge of gaseous oxygen. Hence an increase in temperature will always be favorable so far as the energy consumption is concerned but it is limited by the effects of the last two conditions. With complete oxidation a rise in temperature always acts favorably because it increases the velocity of diffusion of the depolarizer; with incomplete oxidation of substances not easily oxidizable made possible by the overvoltage of oxygen, the reverse may hold because it facilitates the discharge of oxygen. According as one or the other of these two effects predominates it will be better to work at a high or low temperature.

In comparison with Expt. 4, carried out at room temperature, Expts. 13 and 14 were carried out at 10° C. and 55° C., respectively. Curve 4 shows that room temperature (Expt. 4) gives the best results and the yield becomes poorer if the temperature is either raised or lowered. This indicates that at a low temperature the diffusion of chromium ion is too slow to give a good efficiency, while at a high temperature the efficiency is lessened somewhat, probably by the discharge of oxygen.

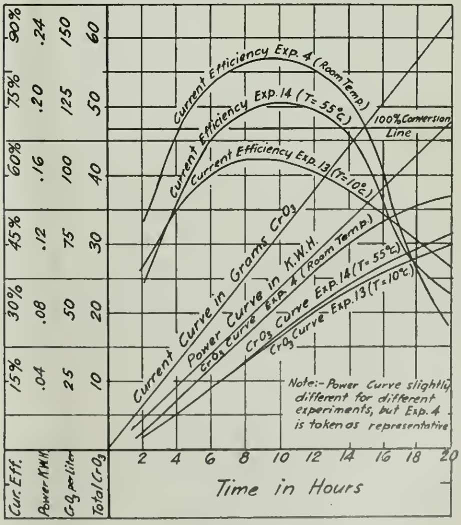
(F) RELATIVE SIZE OF THE CATHODE TO THE ANODE—In electrolysis without diaphragm it is generally known that a high current density at anode and low current density at cathode will be in favor of reduction, while the reverse in favor of oxidation, because the chemical action varies with the electrode surface. In this case, however, the relative size of the cathode to the anode may not make any difference since a diaphragm is provided and the reducing effect of the cathode on the anode liquor is thus prevented.

In order to determine this, Expt. 15 was carried out as in Expt. 12 (current density, 0.5 ampere per square decimeter, room temperature, etc.) except that the cathode size of the former experiment was only one-half that of the latter. As the results show, a decrease in the size of the cathode for the same anode does not make any appreciable difference.

EXPERIMENT	CrO_3 per Liter Grams	Conversion Per cent	Total Current Efficiency Per cent	CrO_3 per k. w. h. Grams
12	91.0	77	72.8	276
15	90.2	76	72.8	293

(G) MATERIAL AND COMPOSITION OF ANODE—An anode to be suitable for the purpose at all must conduct electricity well and must not be attacked chemically or disintegrated to any great extent when in use. Moreover it exerts specific influence in two ways: One in virtue of its oxygen overvoltage, and the other depending on its catalytic influence on the reactions between oxygen and the substance to be oxidized. When dealing with a substance that is only oxidized with difficulty at a very high anodic potential, it is best to use an anode which will increase the overvoltage of oxygen.

In chromic acid regeneration, however, there is not much choice as to what kind of anode will suit the purpose. Nickel and iron will not stand the acid conditions, amorphous carbon or graphite will not work very well under oxidizing conditions, platinum gives practically zero result on oxidation and duriron is attacked by the acid under the experimental conditions. Lead is the only commercially available material which can be readily adapted for this purpose. Furthermore a lead anode forms lead dioxide on the surface, which possibly acts as a catalytic agent between oxygen and the chromic salt. In fact, one author has even said that it is the lead dioxide that actually oxidizes the chromic salt. Hard lead has been used as the anode for these experiments and it has been found satisfactory.



Note:- Power Curve slightly different for different experiments, but Exp. 4 is taken as representative

CURVE 4—TEMPERATURE CURVE

(H) PRELIMINARY TREATMENT OF ORGANIC MATTER—It has already been stated that before every experiment the waste was filtered through a sand filter 2 in. deep in order to remove any suspended organic matter. Incidentally, however, one experiment was carried out under the same conditions as Expt. 4, but gave a much poorer result, especially during the first 4 hrs. Investigation showed that this was due to inefficient filtration of the waste liquor through the sand filter, indicating the importance of this preliminary treatment in the process.

(I) DIAPHRAGM—The lack of a satisfactory diaphragm has probably hindered or prevented the commercial success of many promising electrolytic processes. A diaphragm must not be attacked or disintegrated by the electrolyte, and it must be able to stand mechanical strain well. A frequent renewal or repairing of the diaphragm will involve not only a high expense but also interruption or disturbance of the operations, which must be avoided in commercial work.

Furthermore, a diaphragm must not be permeable to the liquid except by the slow process of diffusion, so that the anolyte and catholyte will not commingle until after a considerable period. In other words, the proper porosity of the diaphragm calls for careful study. On the other hand, a diaphragm material should offer little resistance to diffusion or migration of ions so that the electric resistance will not be so great as to be prohibitory.

All these considerations limit the diaphragm composition to a very few materials which will be available and suitable for electrolytic processes on a commercial scale. In case of chromic acid regeneration, three kinds of diaphragm materials may be considered: Asbestos cloth, porous clay, and electro-filtros. The first few experiments were carried out with an asbestos cloth cup; the rest of the non-continuous experiments with a porous clay cup. The asbestos cloth becomes brittle rather easily due to action of the acid. Porous cups approach nearest to the ideal of what a diaphragm material should be. But they are generally satisfactory for laboratory purposes only, not for large scale operation, as they are not cheap and are not available in commercially useful sizes and shapes at the present time. Electro-filtros proved to be the best diaphragm material to be used in the chromic acid regeneration. It is not appreciably attacked or altered by the solutions and has a rather low electric resistance; it stands mechanical stress well and, under the conditions used, is permeable practically only to diffusing liquids and migrating ions. It is constructed of grains of silica, which are cemented together with a small percentage of a fused siliceous binding material and can be made in many different commercial sizes and shapes. This was the diaphragm used in the continuous runs on a rather large scale.

(K) DISPENSING WITH DIAPHRAGM—As referred to in the literature, attempts had been made to dispense with the use of a diaphragm in the electrolytic regeneration of chromic acid, but careful examination indicates that such attempts could not be successful. The bell jar devised by Le Blanc will not work smoothly because of the fact that in case of chromic acid regeneration the raw waste and the finished solution would not be very different in specific gravity, as they would be in the case of alkaline cells, a condition which is essential for the success of the method.

Another method in dispensing with the use of a diaphragm, as also referred to in the literature, was to use some chemical agents such as sodium acetate, ammonium acetate, etc., in order to reduce the cathodic potential so that it would not interfere with the process of oxidation. This device is not successful either, as the hydrogen gas always comes off at the cathode and the chromic acid produced is reduced by the hydrogen gas to a greater or less extent, no matter how much the cathode potential might be reduced. It means low current efficiency, high energy consumption, and consequently larger cost in use.

(L) CATALYSIS—As reviewed in the literature, there are some chemicals such as potassium fluoride, secondary sodium *o*-phosphate, etc., which may be added as catalytic agents in chromic acid regeneration. These may be helpful in improving the yield of oxidation and consequently reducing the cost of manufacturing. Just to what extent each of these catalytic agents would affect the process of regeneration can be determined only by careful experimentation, and time was not taken to go into these details in the present research.

(M) NATURE OF THE WASTE LIQUOR—All the experiments described so far were carried out with the waste liquor, which was received in September 1918; additional waste liquor was received later. Two experiments were carried out with the second lot of waste liquor, one with a current density of 2 amperes, the other with that of 0.5 ampere per square decimeter.

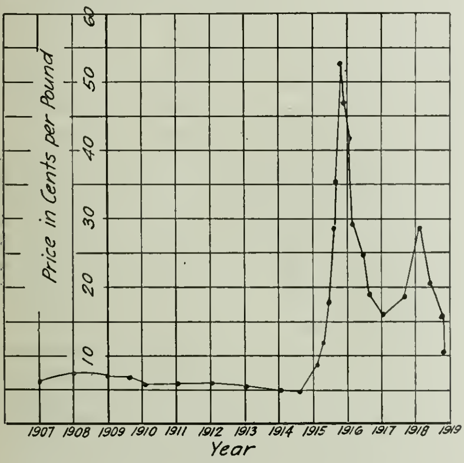
From results of these experiments, it is evident that the second lot required somewhat more electric energy to destroy the organic matter at the beginning of the experiment, because of the greater quantity of organic materials present; after the organic matter was destroyed, it worked about the same as the first lot. Accordingly it gave slightly lower current efficiency, and required slightly higher energy consumption than the first waste for a given per cent conversion of the chromic acid, as shown in the following comparison:

WASTE LIQUOR	C. D. Anode Amps./ Sq. Dm.	Conversion Per cent	CrO_3 per Liter	Current Efficiency	CrO_3 per k. w. h. Grams
First	2.0	77.6	91.7	65.2	221
First	0.5	77.0	91.0	72.8	276
Second	2.0	76.8	85.8	55.0	173
Second	0.5	77.9	87.0	62.3	245

III—CONTINUOUS OPERATION

The last and most important step in solving completely the problem of developing a continuous process for electrolytic regeneration of chromic acid from waste is to work out the conditions under which the process can be carried out in a continuous operation. Thus far only the technical details for the discontinuous part of the process have been worked on. To make the process commercially applicable, however, the market prices and the cost of regeneration of the product must be considered.

The price of sodium bichromate has, of course, fluctuated greatly during the war period and has been dropping since the armistice was signed. Curve 5 shows both the normal prices before the war and the fluctuation during the war period. While it is interesting to note the war fluctuations, Curve 5 shows that the lowest price for sodium bichromate since 1907 is 4.62 cents per pound, which means about six cents per pound of chromic anhydride equivalent. It is probable that the price will be somewhat higher. Thus a fairly stable price after the war for sodium bichromate may be safely estimated at seven to eight cents per pound of chromic anhydride equivalent.



Curve 5—Price Curve for Sodium Bichromate (1907–1919)

From the data obtained by experiments so far, the energy consumption under the most favorable conditions for the first waste is 276 g., and for the second waste 245 g. chromic anhydride per k. w. h. These figures are based upon the chromic acid content of about 80 g. per liter, because it is the value commercially desired for the chromic acid strength before it can be used for oxidation purposes. It means that for the equivalent of every pound of chromic anhydride produced an energy consumption of two k. w. h. is required. At the cost of $30 per h. p. year (0.5 cent per k. w. h.) for the electric energy, the cost for electricity alone in producing equivalent amount of one pound of chromic anhydride will be about one cent. If the cost of power is $60 per h. p. year, the normal figure for generating electricity from steam, the cost for one pound of chromic anhydride equivalent will be about two cents. This does not, of course, take into account power losses, and the costs of installation, labor, repair, and operation.

Labor cost is always a large item, if not the largest, in the cost of manufacture of a product. This is especially true in the case of chromic acid regeneration on a discontinuous operation, because it requires excessive labor in handling, such as charging fresh waste, discharging finished solutions. The labor question cannot be too strongly emphasized, and is the reason why attention should be given to working out a continuous process for chromic acid regeneration.

A continuous operation would permit feeding the fresh waste liquor in at one part and drawing out the finished solution at the other part of the cell, giving a continuous flow of electrolyte. The only interruption would be for replacing the electrodes occasionally. Continuous operation appears very simple but consideration of its technical details reveals many difficulties to be overcome, among which is the adjustment of the sulfuric acid concentrations both at the anode and at the cathode chambers, difficult even on a discontinuous operation, where Le Blanc proposed to exchange the anode and the cathode liquors in each subsequent operation. This will not do for a continuous operation, however, as the anode and cathode liquors cannot be exchanged but must be constant at all times. Otherwise the change in sulfuric acid concentration would develop to such a stage that the process must be necessarily interrupted and some means for modifying the strength applied before the electrolytic oxidation can be resumed.

In the process devised the fresh waste is fed directly into the bottom at one end of the cathode chamber, overflowing through an orifice at the other end of the same chamber into the anode chamber in which the level of the electrolyte is kept slightly lower. The finished solution is then drawn out continuously at the opposite end of the anode chamber, either by a siphon or overflow. In this way not only a continuous flow of electrolyte is insured but also the finished solution can be removed from the cell continuously. Moreover, a complete adjustment of the sulfuric acid concentration is accomplished. The acid concentration in the cathode chamber is restored by feeding in fresh waste, while in the anode chamber it is reduced and balanced by the overflow liquor from the cathode chamber. Thus the sulfuric acid concentration in both chambers will remain practically constant and the continuity of the process assured.

The next technical problem is the construction of the cell, the shape of which is important. For laboratory purposes a beaker or large jar with diaphragm cup inside is naturally the most convenient arrangement, but on a commercial scale a rectangular tank is much preferred because it is not only easier to construct but far more convenient to handle in the plant. The complete arrangement of the cell with both mechanical and electrical connections is shown in Fig. 1. The diaphragm used here is electro-filtros.

The next consideration is the concentration of chromic acid which we wish to maintain in the anode chamber at all times, *i. e.*, the strength of the finished solution. According to ordinary commercial practice a solution of about 70 g. chromic anhydride equivalent is advisable to use as oxidizing agent. Therefore, the anolyte, and consequently the finished solution, in the continuous process should be maintained above this limit.

In accordance with these conditions and arrangements, the first continuous experiment was conducted with the second lot of waste liquor, as follows:

Anode: 7.7 sq. dm.
Cathode: 5.0 sq. dm.
Anolyte: 5000 cc. second waste, containing 200 g. sulfuric acid, and 80 g. chromium oxide per liter.
Catholyte: 550 cc. second waste, with the same content as the anolyte.
Diaphragm: Electro-filtros, 6 × 3 × 12 in. box.
With air circulation.

Hour	Temp. ° C.	Current Amps.	C. D. Anode Amps./ Sq. Dm.	Voltage	Inflow per Hour Cc.	Total Inflow Cc.	Total Outflow Cc.
7th........	23	8	1	4.0	70	490	490
11th........	23	8	1	3.9	55	710	710

The analysis and calculations of the above experiment gave the following results:

	Grams Chromic Anhydride						
	Anolyte Start		Anolyte Finish				
Hour	per Liter	Total	per Liter	Total	CrO_3 Actually Produced Grams	Current	Power CxV
7th...	85.3	426	74.5	410	0.0	70	0.22
11th...	74.5	372	72.8	381	9.0	40	0.13

Hour	Current Efficiency Per cent	CrO_3 per k. w. h. Grams
7th....................	0.0	0.0
11th....................	22.5	70.0

These results show that current efficiency for the first 7 hrs. was zero, while for the last 4 hrs. was only 22.5 per cent, a poor result that may be due to either of the following reasons or both: (*a*) the reducing effect of the cathode on the waste; (*b*) the lack of sufficient chromic salt in the anolyte to produce an efficient depolarization.

(*a*) THE REDUCING DEFECT OF THE CATHODE ON THE WASTE—When the fresh waste liquor is circulated from the cathode chamber to the anode it is quite possible that the organic matter present has been reduced further by the cathode action; thus reduced, it may require much more current to destroy the organic matter present than would be the case in fresh waste; hence it gives a low current efficiency.

Consideration of the possible remedy discovers several methods. One is to avoid cathode circulation, *i. e.*, to feed all the fresh waste liquor directly into the anode chamber instead of passing it first into the cathode compartment. This would be the best and simplest solution of the problem but in view of the importance of the balance of the sulfuric acid concentration it is impossible in continuous operation.

Another method is to reduce the cathode action by decreasing the cathode surface. It will be recalled that the size of the cathode does not make much difference in a discontinuous run, since a diaphragm is provided. But when the effect of further reduction of the organic matter is considered it is clear that decreasing the size of the cathode may hinder cathodic action and consequently reduce the current losses. Thus the decrease of the cathode surface may have a direct bearing on the subject.

(*b*) THE LACK OF SUFFICIENT CHROMIC SALT IN THE ANOLYTE TO PRODUCE AN EFFICIENT DEPOLARIZATION—It has been pointed out that the lower the ratio of the chromic salt to the chromic acid, the lower will be the current efficiency. This is perhaps the reason why the result of the first 7 hrs. in the above experiment was far worse than that of the last 4 hrs.

One of the possible ways to overcome this difficulty is to divide the process into two or more steps, *i. e.*, first to oxidize the waste to about 40 g. chromic anhydride per liter, and then to oxidize the latter to the finished solution of the desired chromic anhydride content, say 70 g. per liter. In this way most of the chromic anhydride will be produced at comparatively high current efficiency and only a small fraction of it at low current efficiency, *i. e.*, the average current efficiency will be much increased.

But any chromic anhydride in the solution is completely reduced while passing through the cathode chamber. In the oxidation of the solution containing about 40 to 50 g. chromic anhydride per liter to a solution of 70 g. per liter, the former solution cannot be fed through the cathode chamber first, consequently the sulfuric acid concentration is not balanced and the process is again not continuous.

Another method is to add chromic salt to the anode liquor at the beginning so as to increase the ratio of this salt to the chromic anhydride or to use a waste liquor of higher chromic salt content at the start.

While it may be disadvantageous to concentrate the waste by evaporation, as said before, it might not be at all inconvenient to use a solution of high chromic acid content as the oxidizing agent, so that the waste liquor will be always high in chromic salt content. Therefore, this will be the best for furnishing enough chromic salt in the anode liquor to insure efficient oxidation.

On these two methods, (*a*) the decrease in cathode surface, and (*b*) the use of a solution of high chromic salt content in the anode chamber at the start, are based the following experiments, carried out with the same waste liquor (second lot) and with other conditions as in the previous experiment, except the decrease in cathode surface (two small cathodes, 10 × 6 = 60 sq. cm. each, instead of one large cathode, 10 × 25 = 250 sq. cm.).

Hour	Temp. ° C.	Current Amps.	C. D. Anode Amps./ Sq. Dm.	Voltage	Inflow per Hour Cc.	Total Inflow Cc.	Total Outflow Cc.
4th....	25	10	1.2	4.6	70	280	280
11th....	30	10	1.2	4.4	70	770	770
19th....	31	10	1.2	4.4	70	1330	1330

The analysis and calculations of this experiment gave the following results:

	Grams CrO_3			
	Anolyte Start		Anolyte Finish	
Hour	per Liter	Total	per Liter	Total
4th............	73.8	368	73.8	389
11th............	73.8	368	73.8	405
19th............	73.8	368	73.8	409

Hour	CrO_3 Actually Produced Grams	Current	Power C x V	Current Efficiency Per cent	CrO_3 per k. w. h Grams
4th.....	21.0	50.0	0.184	42.0	114
11th.....	37.0	87.5	0.313	42.5	117
19th.....	41.3	100.0	0.352	41.3	117

The result of this experiment with decreased cathode surface is better than that in the previous experiment.

The following experiment was conducted with the first lot of waste liquor, with all conditions as in the above experiment except that the chromic salt content in the solution was higher (total chromium oxide equivalent 96 g. per liter instead of only 80 g.).

Hour	Temp. ° C.	Current Amps.	C. D. Anode Amps./Sq. Dm.	Voltage	Inflow per Hour Cc.	Total In-flow Cc.	Total Out-flow Cc.
10th....	25	10	1.2	4.5	100.0	1000	1000
32nd....	20	10	1.2	4.6	83.3	3000	3000
57th...	25	10	1.2	4.5	90.7	5000	5000

The analysis and calculations of this experiment gave the following results:

	H_2SO_4 per Liter		Grams CrO_3			
			Anolyte Start		Anolyte Finish	
Hour	Anode	Cathode	per Liter	Total	per Liter	Total
10th........	475	194	70.5	352	67.2	403
32nd........	424	151	67.2	337	67.2	403
57th........	388	152	71.4	356	73.0	437

Hour	CrO_3 Actually Produced Grams	Current	Power C x V	Current Efficiency Per cent	CrO_3 per k. w. h. Grams
10th........	51	125.0	0.45	40.8	113
32nd........	79	150.0	0.55	52.7	143
57th........	81	137.5	0.495	59.0	163

It is apparent from the above tables that the results with the stronger liquor are very good. A superficial examination may give the impression that the results obtained in this experiment on a continuous operation are not quite so good as those in a discontinuous run. But we must remember that all the discontinuous experiments were carried out with entirely fresh waste liquor, and all the cathode liquors were discarded. If we should try to regenerate the chromic acid from the cathode liquors as well as from the fresh waste, which would be necessary in commercial practice, the results in a discontinuous run would probably be no better than those obtained in the continuous operations. Hence, the above experiment is entirely satisfactory in every respect; the current efficiency rather high; the energy consumption low; the chromic acid content of the finished solution up to commercial standard, and, most important of all, the sulfuric acid concentration in both chambers practically constant.

This experiment evidenced that the efficiency of the process is usually low at the beginning, gradually increases, and then comes to a constant value. This is probably due to the fact that time is required for the formation of lead dioxide which is to serve as a surface catalyzer. As emphasized before, the conditions are such that the less the experiment is interrupted the better. Hence, the continuous process is especially desirable because it insures no interruption for a long time.

In order to find out the results which the second waste would give on a constant long run, the above experiment was continued with the feeding in of the second waste liquor instead of the first with the following results:

Hour	Temp. ° C.	Current Amps.	C. D. Anode Amps./Sq. Dm.	Voltage	Inflow per Hour Cc.	Total In-flow Cc.	Total Out-flow Cc.
11th........	26	10.3	1.2	4.2	90	1000	1000
35th........	27	10.0	1.2	4.5	83	3000	3000
59th........	30	10.0	1.2	4.3	83	5000	5000
83rd........	31	10.0	1.2	4.3	83	7000	7000

The analysis and calculations gave the following results:

	H_2SO_4 per Liter		Grams CrO_3			
			Anolyte Start		Anolyte Finish	
Hour	Anode	Cathode	Per Liter	Total	Per Liter	Total
11th........	368	158	73.0	365	72.2	432
35th........	352	144	72.2	361	73.0	438
59th	338	122	73.8	369	73.8	442
83rd			73.8	369	74.6	448

Hour	CrO_2 Actually Produced Grams	Current	Power C x V	Current Efficiency Per cent	CrO_3 per k. w. h. Grams
11th.........	67	142	0.476	47.2	141
35th.........	77	150	0.540	51.2	142
59th	73	150	0.516	48.7	141
83rd.........	79	150	0.516	52.6	152

From the above table, it is clear that the results for the second waste on a continuous operation are practically as good as those from the first waste, though the current efficiency is lower, due, apparently, to the presence of more organic matter in the second waste liquor than in the first.

To gauge the effect of higher current density, the above experiment was continued with a current density of 2.4 instead of only 1.2 amperes per sq. dm. The following results show that the energy consumption is much higher on account of lower current efficiency and greater voltage. However, it must be noted that the capacity of the cell is somewhat increased.

Hour	Temp. ° C.	Current Amps.	C. D. Anode Amps./Sq. Dm.	Voltage	Inflow per Hour Cc.	Total In-flow Cc.	Total Out-flow Cc.
6th.........	40	20	2.4	5.7	165	1000	1000
12th.........	40	20	2.4	5.7	165	2000	2000

The analysis and calculations gave the following results:

	H_2SO_4 per Liter		Grams CrO_3			
			Anolyte Start		Anolyte Finish	
Hour	Anode	Cathode	Per Liter	Total	Per Liter	Total
6th......	330	122	74.5	373	67.5	405
12th......	350	122	73.1	366	67.8	407

Hour	CrO_3 Actually Produced Grams	Current	Power C x V	Current Efficiency Per cent	CrO_3 per k. w. h. Grams
6th........	32	150	0.685	21.0	46.7
12th........	41	150	0.685	27.3	60.0

For a given current density the capacity of the cell is directly proportional to the anode surface. For a current density of 1.2 amperes per sq. dm., about one-third of a pound of chromic anhydride equivalent is produced in 24 hrs. for an anode surface of 8 sq. dm.; for a current density of 2.4 amperes per sq. dm., about four-elevenths of a pound is produced in 24 hrs. for the same anode surface.

CONCLUSIONS

Consideration turns to the economic aspect of the process in a continuous operation. At a current density of about 1.2 amperes per sq. dm., the first waste can be regenerated at a current efficiency of about 59 per cent and an energy consumption of about 160 g. chromic anhydride equivalent per k. w. h., and the second waste regenerated at a current efficiency of about 50 per cent and an energy consumption of about 140 g. per k. w. h. In other words, for every pound of chromic anhydride equivalent regenerated, about three k. w. h. of electric energy will be required. At a rate of $30 per h. p. year (0.5 cent per k. w. h.) the regeneration of chromic acid by this process costs for electric current only two cents per pound of chromic anhydride equivalent regenerated. By virtue of its continuous operation, it dispenses with excessive labor and costs production. With chromic acid at 7 to 8 cents per pound, there remains a good margin of profit on the process. Furthermore, sulfuric acid is also regenerated in the process without additional cost. This means a saving of about four pounds of sulfuric acid for every pound of chromic anhydride equivalent regenerated. With sulfuric acid at $14 per ton, this would amount to about three cents for every pound of chromic acid regenerated. Accordingly the continuous process thus developed for the electrolytic regeneration of chromic acid from waste liquor gives promise of valuable technical applications.[1]

SUMMARY

Results obtained in the foregoing paper on developing a continuous process for electrolytic regeneration of chromic acid from waste liquor may be briefly summarized as follows:

I—It has been found possible simply by the action of the electric current to destroy the organic matter in waste chromium liquor without subjecting it to any preliminary treatment.

II—Conditions have been worked out, under which the process of regeneration can be conducted successfully as a continuous operation, *i. e.*, the fresh waste liquor is fed in at one part, and the finished solution drawn out at the other part of the cell without interruption. Careful adjustment of conditions and arrangements give good results: current efficiency fair, energy consumption low, chromic acid content of the finished solution up to commercial standard, and, most important of all, sulfuric acid concentration in both chambers practically constant.

It has been found that for every pound of chromic acid regenerated only about 3 k. w. h. of electric energy are required. Furthermore the saving of sulfuric acid, which is also regenerated in the process without additional cost, will amount to nearly as much as the cost of electric energy required (at one cent per k. w. h.) for the regeneration of the chromic acid.

DETERMINATION OF THE WATER RESISTANCE OF FABRICS[2,3]

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Received July 9, 1919

The waterproofing of canvas to be used as coverings for outdoor use has long been practiced, but the World War has naturally increased its importance not only for protective purposes but also as a means of prolonging the usefulness of canvas coverings and thus decreasing the expense of using them. In developing simple and effectual formulas and treatments for waterproofing canvas, both for small scale application with a brush or as a spray and for application in large treating plants, and for testing deliveries of commercially waterproofed fabrics, it has been found necessary to develop practical and simple laboratory tests by which the effectiveness and probable durability of the waterproofing treatment may be judged.

A number of methods have been proposed for testing the water resistance of fabrics. All of them, however, have been applied to the new material without any effort even to remove the first purely transitory resistance, and, furthermore, the literature on the subject does not reveal comparative studies of the value of the several tests. The results obtained by the different methods have not been satisfactorily standardized, nor have the results of laboratory tests apparently been coördinated with the behavior of fabrics exposed to actual weathering or service tests.

Gawalouski[1] describes an apparatus for testing the water resistance of fabrics by attaching a piece of cloth to an open end of a graduated tube such as a burette and filling it with a column of water 12 in. in height. The water dripping through is collected in a graduated measuring glass. He tested a large number of fabrics and found that many allowed from 1 to 6 cc. of water to pass through in 5 hrs., while others required 16 to 23 hrs. to collect this quantity. Other samples allowed sufficient water to pass in 5 hrs. to fill the collecting cylinder.

Dannerth[2] describes a method for testing the water resistance by stretching and securely fastening a 2$^1/_2$ in. square of the fabric across the mouth of an ordinary thistle tube. The tube is filled with distilled water at 20° C. and the amounts of water that pass through in 5 hrs. and 10 hrs., respectively, are measured. A fabric which allows no water to pass through in 10 hrs. is considered first class. A high grade cravenette allowed all the water to pass through in 5 hrs. Drops of water were visible on the outside of the sample 15 min. after starting the test. With a medium quality "raincloth" the outer surface of the fabric had become damp after 5 hrs. After 10 hrs. half of the water had passed through. With an umbrella cloth no water passed through in 10 hrs.

Heermann[3] described several methods:

BAG TEST—A square of the fabric, 50 × 50 cm., or 100 × 100 cm., is tied with strings by the four corners to a frame in such a way that a bag is formed. The bag is filled to a given height with water at the temperature of the room. The height of the column of water used varies, depending on the uses to which the fabric is to be put. No dropping or trickling through of water should take place in 24 hrs., but sweating through or transudation is permitted.

Uniform cloth, tent cloth, fabric for knapsacks and bread bags were tested by this method, using pieces 50 cm. square, filled with water to a depth of 75 mm. After 24 hrs. the water may sweat through but should not drip through. The specifications for wagon covers for the Prussian State Railways prescribed that a piece 100 cm. square should be used and that the depth of water should be 10 cm. After 24 hrs. there should be no dripping. Heermann considers one test as usually sufficient but in certain circumstances the same piece is dried and tested for a second or third time, in order to determine how the fabric stands wear.

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[1] U. S. Patent Application 321,609.

[2] Acknowledgment is made to H. P. Holman and B. S. Levine, of the Leather and Paper Laboratory, Bureau of Chemistry, U. S. Department of Agriculture, for valuable assistance in developing the methods and equipment.

[3] Read at the 57th Meeting of the American Chemical Society, Buffalo, N. Y., April 7 to 11, 1919.

[1] *Leipziger Monatschrift*, **1893**, 221; also "Textile Fibres," Matthews, p. 573, John Wiley & Sons, 1913; and "Technical Testing of Yarns and Textile Fabrics," Herzfeld, p. 155, Scott, Greenwood & Son, 1902.

[2] *Textile World Record*, **34** (1908), 630; "Methods of Textile Chemistry," Dannerth, p. 53, John Wiley & Sons, Inc., 1908.

[3] *Mechanisch- und Physikalisch-Technische Textiluntersuchungen, Berlin*, **1912**, 232–239.

BURETTE TEST—This test is similar to Dannerth's described above.

FUNNEL TEST—A piece of the cloth to be tested is folded like a paper filter, placed in a glass funnel, and 300 cc. of water are poured into the cloth filter thus formed. Waterproof fabrics should not wet through in 24 hrs.; the outer side should show only regularly spaced drops.[1]

WATER PRESSURE TEST—The pressure at which the water begins to penetrate the fabric is determined. The time in which water passes through the cloth at a constant pressure can also be determined with the apparatus. The apparatus used is fully described by Heermann.

SPRAY TEST—A piece of cloth 50 × 50 cm. is weighed after having been exposed to 65° relative moisture for several hours. It is then spread out smoothly on a frame and set up outdoors in a slanting position. A sprinkling apparatus connected with the water supply is set up at a distance of 6 to 10 meters from the cloth, the nozzle of which is arranged so that a fine spray strikes the goods perpendicularly and equally all over and falls from a height of 2 or 3 meters. The under surface is examined from time to time for penetration of water. If the water has not penetrated the spraying is continued. Whether, and at what time, water appears on the under side during the spraying is also observed. At the end of an hour the spraying is stopped, the material is hung up to dry for 5 min. and weighed. It is claimed that the smaller the amount of water absorbed the more efficient is the waterproofing preparation. Duplicate or triplicate tests are made.

Wosnessensky[2] describes an instrument for measuring the degree of impermeability of cloth based upon the number of hammer strokes before the water percolates through, the cloth being pressed upward by a column of water.

Villavecchia[3] describes a spray test in which the fabric is inclined at an angle of 25° and water allowed to drip upon it for 3 hrs. from a height of 2 meters at a rate of 3 l. per min. on the central part of the fabric so as to cover an area of 3 cm. in circumference. At the end of the experiment no water, or at most a minimum quantity, should have penetrated the fabric.

LeRoy[4] determines the degree of impermeability of fabrics to still water and imitation rain.

Clark[5] stretches a piece of fabric over a wide-mouth bottle and allows a heavy artificial rain from a Gooch crucible attached by means of a cork and a tube to a faucet to fall upon it.

Clark also folds a piece of fabric into a pocket into which some heavy articles are placed and immerses as far as possible in water. A resistant fabric should not wet through in 24 hrs.

DEVELOPMENT OF METHOD

From a consideration of the numerous procedures heretofore proposed, it appeared that the funnel test and the spray test could be standardized to be simple in operation and at the same time furnish definite information as to the effectiveness of the waterproofing treatment of the fabric. The elimination of additional tests is much to be desired. The new features which have been introduced materially extend the information obtained and increase the reliability of the results as a basis for judging the resistance of the fabric in service.

The details of the methods as finally developed follow.

MODIFIED FUNNEL TEST—Cut a piece of the fabric one foot square, weigh, crumple thoroughly in the hand and place in an 800-cc. beaker and soak in distilled water at from 70° to 80° F. for 24 hrs., removing, straightening out and recrumpling 4 or 5 times during this period. Remove from the water, straighten out and dry in oven at 45° C. for 24 hrs. Hang in laboratory over night. Crumple, resoak in distilled water, and dry at 45° C. for 24 hrs. and hang in laboratory over night as before. Again crumple, smooth out and place on a piece of absorbent paper (paper toweling) of the same size and fold the two together into the form of a filter, insert in a 6-in. glass funnel having an angle of 60°, and place the funnel in a support[1] (Fig. 1) over a 500-cc. graduated glass cylinder and fill the funnel to a depth of exactly 4 in. with distilled water of 70°–80° F. This depth equals 500 cc. of water. Maintain a constant water level above the funnel by inverting an Erlenmeyer flask filled with water and closed with a rubber stopper through which passes a glass tube ground at the end to an angle of 45°.

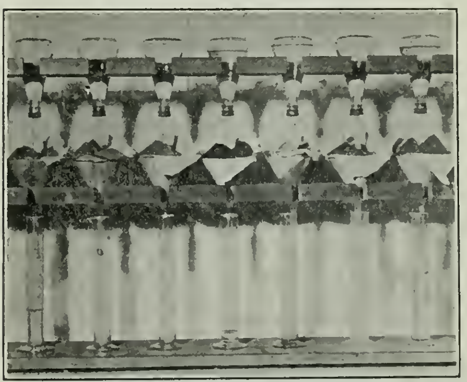

FIG. 1

Make the following observations:

1—The time elapsed before the paper begins to wet.

2—The time elapsed until the paper is entirely wet.

3—The time elapsed before the first drop passes into the cylinder.

4—The quantity of water in the cylinder in 1, 3, 6, and 24 hrs.

5—The time and extent to which the fabric becomes wet above the water level.

At the expiration of 24 hrs., if there has been no dripping, the funnel filled with water is lifted 2 in. and allowed to drop into its support; this is repeated four times and the amount of water that drips through in 3 hrs., if any, is recorded.

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[1] This is probably the test described by Matthews and Herzfeld (*Loc. cit.*) as the test prescribed in the official regulations of the German Clothing Department for testing sailcloth.

[2] *J. Soc. Dyers and Colourists*, **32** (1916), 246.

[3] "Applied Analytical Chemistry," 2, p. 521, P. Blakiston's Sons & Co., 1918.

[4] *Ann. fals.*, **85** and **86** (1915), 377.

[5] *Textile World J.*, **53** (1918), 43.

[1] This support is made of wood, holding ten funnels 6 in. in diameter.

Remove the funnel from its support and carefully pour and drain off the water, and then remove the fabric and paper from the funnel, smooth out, and observe:

1—Whether the paper is dry, damp or wet.

2—Whether the fabric on the outside is dry, damp or wet, or whether the water has only sweated through.

The water resistance of fabrics as determined by this method is rated in accordance with the following scale:

Very High 10	The fabric does not become wet above the water level within 24 hrs. No water drips through. No sweating through is apparent except to a very limited extent at the folds. Filter paper under the fabric remains dry, except for slight wetting where the fabric is folded.
High 9	The fabric does not wet above the water level within 24 hrs. Sweating through is sufficiently rapid to cover generally, and especially in the fold, the outside of the fabric with droplets. Filter paper under the fabric becomes wet.
High-Medium 7 and 8	The water dripping through: In 6 hrs. is from 1 cc. to 5 cc. In 24 hrs. is from 1 cc. to 25 cc. In 3 hrs. after raising and allowing the funnel to drop into support 5 times.
Medium 5 and 6	The water dripping through: In 6 hrs. is from 5 to 25 cc. In 24 hrs. is from 25 to 50 cc.
Medium-Low 3 and 4	The water dripping through: In 6 hrs. is from 25 to 75 cc. In 24 hrs. is from 50 to 150 cc.
Low 1 and 2	The fabric wets above the water level readily. The water dripping through: In 6 hrs. is from 75 to 200 cc. In 24 hrs. is from 150 to 300 cc.
Negligible 0	The water dripping through in 24 hrs. exceeds 300 cc.

MODIFIED SPRAY METHOD—Dry the piece of fabric used in conducting the funnel test at 45° C. for 24 hrs., hang in laboratory over night and clamp loosely in a frame. Set the frame in a holder attached to a trough at an angle of 45°. The trough used held six frames (Fig. 2). Allow clear tap water at room temperature to fall from a height of 6 ft. upon the central portion of the fabric, covering an area of about 8 in. in circumference, for 24 hrs., from a $2^3/_4$ in. brass spray nozzle having 25 holes, each 1.9 (0.75 in.) mm. in diameter, at a rate of 1000 cc. per min.

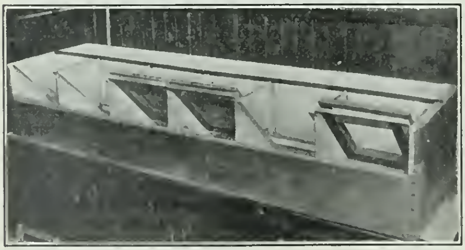

FIG. 2

Inspect the condition of the under side of the fabric at the end of 5 min., $^1/_2$ hr., 1 hr., 3 hrs., 7 hrs., and 24 hrs. Note at each inspection whether the under surface is dry, damp or wet with no dripping; damp or wet with dripping.

The water resistance of fabrics as determined by the modified spray test is rated on a scale of 10 as follows:

10 Undersurface of fabric remains dry for 24 hrs.
9 Undersurface remains dry for 7 hrs. but is damp or wet in 24 hrs. No dripping
8 Undersurface remains dry for 7 hrs. but is damp or wet in 24 hrs. Dripping
Undersurface remains dry for 3 hrs. but is damp or wet in 7 hrs. No dripping
7 Undersurface remains dry for 3 hrs. but is damp or wet in 7 hrs. Dripping
6 Undersurface remains dry for 1 hr. but is damp or wet in 3 hrs. No dripping
5 Undersurface remains dry for 1 hr. but is damp or wet in 3 hrs. Dripping
4 Undersurface remains dry for $^1/_2$ hr. but is damp or wet in 1 hr. No dripping
3 Undersurface remains dry for $^1/_2$ hr. but is damp or wet in 1 hr. Dripping
2 Undersurface remains dry for 5 min. but is damp or wet in $^1/_2$ hr. No dripping
1 Undersurface remains dry for 5 min. but is damp or wet in $^1/_2$ hr. Dripping
0 Undersurface damp to dripping in 5 min.

DISCUSSION OF GENERAL PRINCIPLES

MODIFIED FUNNEL TEST—Canvas for covering equipment, wagons, etc., is often bent in various ways or may be folded in short points. The crumpling, wetting, drying, rewetting, and redrying are carried on because in this way the temporary resistance of new fabric is partly removed, and the conditions of actual service are imitated to some definite extent, at least. The paper behind the fabric serves a double purpose of imitating the effect of contact with an absorptive material while the fabric is wet, and, furthermore, promptly shows any wetting through of the fabric.

TABLE 1—COMPARISON OF THE FUNNEL AND THE SPRAY TESTS WITH ACTUAL EXPOSURE TO RAIN

Number	Funnel Test Rating	Spray Test Rating	Actual Rain Test (Condition of Blotting Paper)
32340	0	0	Wet
32745	0	0	Wet
33253	0	0	Wet
33330	0	0	Wet
33433	0	0	Wet
33676	4	2	Wet
33886	0	0	Wet
33965	0	4	Wet
34751	0	0	Wet
34772	0	0	Wet
34780	0	0	Wet
34791	0	0	Wet
34792	0	0	Wet
34964	0	2	Wet
35261	0	0	Wet
35729	0	0	Wet
35730	0	0	Wet
35731	0	0	Wet
35756	0	0	Wet
33617	0	4	Dry
34748	9	9	Dry
34749	10	7	Dry
34810	4	9	Dry
34824	10	9	Dry
34826	4	8	Dry
34828	10	8	Dry
34831	9	9	Dry
34856	0	6	Dry
35737	0	9	Dry

In order to obtain consistent and reliable results by this method, it is necessary to follow closely the directions as outlined, especially as to drying in the oven at 45° C. (113° F.) for 24 hrs. Many comparisons have been made on samples of various treatments by (1) soaking and drying in the air in the laboratory for 24 hrs. and (2) by drying in the oven at 45° C. for 24 hrs. The results show a low water resistance on many samples when dried in air only, and a high water resistance when dried in the oven at 45° C. In no case has the reverse been true.

Table II—Data on the Water Resistance of a Treated Cotton Duck

				Condition of Dry Fabric				Water Resistance		Water Absorption	
Number	Method of Application (Brushed)	Applied Per cent	Pin Holes	—10° C. for 24 Hours	Room Temperature	45° C. for 24 Hours	Condition of Wet Fabric	Funnel Test Rating	Spray Test Rating	Water Absorbed Per cent	Decrease in Water Absorbed Due to Treatment Per cent
36095[1]	Used as blank	....	Numerous	....	....	....	....	0	2	61.0	....
36164	1 coat on each side	34.2	Numerous	Satisfactory	Satisfactory	Satisfactory	Slightly sticky	7	6	33.0	46.0
36164	2 coats on one side	36.4	Several	Satisfactory	Satisfactory	Satisfactory	Slightly sticky	9	8	32.0	46.0
36166	1 coat on each side	33.5	Numerous	Stiffens slightly	Satisfactory	Satisfactory	Slightly sticky	10	10	30.0	51.0
36166	2 coats on one side	34.9	Several	Stiffens slightly	Satisfactory	Satisfactory	Slightly sticky	9	10	31.0	49.0
36168	1 coat on each side	30.0	Numerous	Stiffens slightly	Satisfactory	Satisfactory	Slightly sticky	10	9	33.0	46.0
36168	2 coats on one side	34.9	Several	Stiffens slightly	Satisfactory	Satisfactory	Slightly sticky	10	9	32.0	48.0
36170	1 coat on each side	34.9	Several	Stiffens slightly	Satisfactory	Satisfactory	Slightly sticky	7	9	29.0	50.0
36170	2 coats on one side	34.9	None	Stiffens slightly	Satisfactory	Satisfactory	Slightly sticky	8	9	30.0	51.0
36172	1 coat on each side	35.7	Several	Satisfactory	Satisfactory	Satisfactory	Slightly sticky	8	9	28.0	54.0
36172	2 coats on one side	41.3	None	Satisfactory	Satisfactory	Satisfactory	Slightly sticky	9	9	30.0	51.0
36174	1 coat on each side	32.8	Several	Stiffens slightly	Satisfactory	Satisfactory	Satisfactory	9	10	30.0	51.0
36174	2 coats on one side	28.6	Numerous	Stiffens slightly	Satisfactory	Satisfactory	Satisfactory	10	10	32.0	48.0
36176	1 coat on each side	25.8	Numerous	Stiffens slightly	Satisfactory	Satisfactory	Satisfactory	10	9	33.0	46.0
36176	2 coats on one side	17.9	Numerous	Stiffens slightly	Satisfactory	Satisfactory	Satisfactory	10	9	33.0	46.0
36178	1 coat on each side	34.2	Numerous	Stiffens	Stiffens slightly	Satisfactory	Satisfactory	10	10	31.0	49.0
36178	2 coats on one side	30.8	Numerous	Stiffens	Stiffens slightly	Satisfactory	Satisfactory	10	10	34.0	44.0
36180	1 coat on each side	33.5	Numerous	Stiffens	Satisfactory	Satisfactory	Satisfactory	9	9	31.0	49.0
36180	2 coats on one side	33.5	Numerous	Stiffens	Satisfactory	Satisfactory	Satisfactory	9	9	30.0	51.0
36182	1 coat on each side	27.9	Numerous	Stiffens slightly	Satisfactory	Satisfactory	Satisfactory	9	10	32.0	48.0
36182	2 coats on one side	29.3	Numerous	Stiffens slightly	Satisfactory	Satisfactory	Satisfactory	9	10	34.0	44.0
36140	1 coat on each side	34.2	Several	Stiffens	Satisfactory	Satisfactory	Rubs off slightly	8	10	30.0	51.0
36140	2 coats on one side	36.0	Several	Stiffens	Satisfactory	Satisfactory	Rubs off slightly	10	10	32.0	48.0
36229	1 coat on each side	22.4	None	Stiffens considerably	Stiffens slightly	Satisfactory	Stiffens slightly	0	10	40.0	34.0

[1] Untreated cotton duck used for all treatments. Weight, 14.3 ounces per sq. yd. Threads per inch: warp, 36 (double threads, each one ply); filling, 24 (single threads, one ply).

While it is realized that this test as conducted in this laboratory is a severe one, no canvas which withstands it has been found to fail in actual service.

MODIFIED SPRAY TEST—The spray test establishes, approximately at least, in what time hard rain will penetrate the fabric when it is placed in a slanting position.

Important features of this method are: (1) the rate of flow of water is definitely established and controlled; (2) the water is not subject to uncontrollable fluctuations of pressure; and (3) the temperature of the water remains about the same at all times.

A few typical results in which the funnel and spray tests are compared with an actual rain test on samples which have been exposed to the weather for several months are given in Table I. The actual rain test was carried on by securely attaching a 12-in. square sample flat on the board. Between the board and the fabric was placed a piece of blotting paper. The board on which the fabrics were attached was exposed at an angle of 30° to a gentle continuous rain for 6 hrs. At the end of the rain the blotting paper was examined, with the results recorded in Table I.

The results in Table I show that both the funnel and spray tests give a rating of zero on all except three of the samples under which the blotting paper became wet during the actual rain test. On samples that did not wet through during the same rain, the funnel test ratings range from zero to 10, and the spray test ratings range from 4 to 9.

It will be noted that several of the fabrics which did not become wet on the undersurface during this rain showed a rating of zero by the funnel test. On the other hand, whenever the fabric proved of no value on actual exposure to weather conditions, it has always had a low rating by the funnel test.

The spray test appears to check better with the results obtained by exposure to an actual rain than the funnel test.

In Table II are reported some results by the funnel and spray tests on fabrics treated by formulas developed in this laboratory. The percentage of water absorbed, determined by the method outlined below, is also recorded.

All except one of the treatments herewith reported show a rating of 7 to 10 by the funnel test. This treatment gave a rating of zero.

The spray test gives a rating of 6 to 10 on all samples, the lowest (36164) corresponding to the lowest by the funnel test.

The water absorption of the fabrics was determined as follows:

Dry the sample used in the funnel and spray tests for 24 hrs. at 45° C., weigh, and lay flat in distilled water at a temperature of 70° to 80° C. for 5 hrs., remove, hold by two corners and give it four vigorous, snappy swings by hand; place between two sheets of 50-pound blotting paper on a flat surface, cover with a flat surfaced weight 13 in. square and weighing 5 lbs. Allow to remain under this weight for 30 sec., remove, weigh immediately, and calculate the per cent of water absorbed.

The percentage decrease in water absorbed due to the treatment on all samples herewith reported, while considerable, does not vary to any great extent. The difference is within the error of manipulation, except treatment 36229. This sample shows a percentage decrease in comparison with the untreated cloth of 34 per cent, while all the other treatments range from 44 to 54 per cent. These results confirm a more extended series on the same subject. It is interesting to note also that this treatment (36229) has a rating of zero by the funnel test.

The pressure test essentially as described by Heermann, the water being applied from a height of 20 in., to the undersurface of a circular area of fabric ($2^{3}/_{4}$ in. in diam.), was also studied. The results, however, added nothing to the information supplied by the funnel and spray tests, and it was abandoned.

Other tests and observations made on fabrics which have been treated to increase the water resistance are briefly as follows:

Pin holes: The fabric is held before an electric light, and pin holes are rated as numerous, several, or none.

Condition of the dry fabric at —10° C., at ordinary room temperature and at 45° C. is rated as stiff, or supple, and as greasy, sticky, or rubs off.

Condition of the wet fabric is rated as stiff, or supple, and as greasy, sticky, or rubs off.

A reaction to litmus paper of the water extract is noted.

The sulfates are tested for.

Weight per square yard in ounces is determined before and after washing.

Threads per inch, warp and filling are counted.

Percentage of ash, qualitative tests for lead, zinc, copper, chromium, aluminum, and iron are determined when desirable.

Quantitative determination of copper is also made when put in mildew-proof fabrics.

An attempt is also made to determine the nature of the waterproofing material as well as the quantity present.

SUMMARY

The modified funnel test and the modified spray test when conducted under the standardized conditions described are simple of execution, give results within a reasonable time, and yield more information on the water resistance of cotton duck than the other tests which have been tried in the Bureau of Chemistry.

ADDENDUM

Since the presentation of this paper at the meeting of the AMERICAN CHEMICAL SOCIETY at Buffalo, April 7 to 11, 1919, there has appeared an article by Martin and Wood[1] entitled "Notes on the Quantitative Testing of Rainproof and Waterproof Cloth." These writers review briefly the various methods for determining the waterproof value of cloth, including the "drop test," "dash test," "trough or bag test," "filter test," "thistle tube test," and the Gawalouski apparatus. These methods, with the exception of the "drop test" and the "dash test" have already been reviewed in this paper. The "drip test" according to Martin and Wood is known as the "War Office test" and it is claimed that it is especially valuable, "in that it furnishes a fairly accurate numerical value of the degree of waterproofing."

The authors describe the "drop test" in which water is allowed to drip from a burette from a height of about 5 ft. at a rate of 20 drops per minute on to the fabric. The cloth is placed at an angle of 45° under which is laid a piece of white blotting paper. The dripping of water is continued until the water passes through the cloth and stains the blotting paper.

A similar test to this has been given a trial in this laboratory but it was discontinued for the spray test because it was believed the latter imitates much better the conditions of an actual rain. The drop test as described by Martin and Wood was, no doubt, devised for waterproofed garments and not for waterproofed cotton duck.

The "dash test" as described consists of holding the fabric horizontally and pouring water on it. Martin and Wood do not consider it of any particular value.

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[1] *J. Soc. Chem. Ind.*, **38** (1919), 84-T.

UTILIZATION OF ASPHALTIC BASE ACID SLUDGE OBTAINED IN REFINING PETROLEUM AND SHALE OILS[1]

By Charles Baskerville

DEPARTMENT OF CHEMISTRY, COLLEGE OF THE CITY OF NEW YORK, NEW YORK CITY

Received July 23, 1919

At certain stages in the process of refining petroleum and shale oils after treatment with sulfuric acid the "acid sludge," as it is usually called, is cooked up by means of live steam, with concentrated sulfuric acid to separate any refinable oil retained by the usually pasty mass and to carbonize the remaining material. This is the common method of disposing of a residuum obtained in large amounts in oils especially of an asphaltic, or partially asphaltic base nature.

The process above outlined may be regarded as taking place in two stages, although they so merge one into the other that it, as practiced, appears as one. As the temperature of the mixture of acid sludge and acid is raised the retained oil escapes from the pasty mass, which becomes quite liquid with the elevation of temperature. The separated oil rises on top of the original mixture. This is effected within about an hour or an hour and a half. The raising of the temperature by means of steam is continued and the acid sludge and concentrated sulfuric acid are mixed intimately. This treatment is continued for several hours longer during which time the refuse or residuum (middle portion) becomes more or less decomposed and carbonized as shown by its change in character and the constant escape of sulfur dioxide, the latter being due to the reduction of sulfuric acid. On ceasing the agitation, the carbonized acid sludge and excess of concentrated acid used separate into two layers, the concentrated sulfuric acid being the bottom layer. The sulfuric acid is drawn from beneath to be used again, and the acid sludge thus produced is run out into a suitable conveyor trough and washed once with water, whereby usually about one-half of the retained acid is removed and is sometimes recovered. This washed, acid-cooked residue is usually burned with coal to get rid of it. It contains from 3 to 15 per cent of free sulfuric acid.

Many investigations have been carried out looking toward utilization of this cooked acid sludge, but the most economical practice to date appears to be its destruction by burning. Its production involves large and expensive lead-lined kettles and its disposition entails much labor. In fact, it is a nuisance to the refiner of petroleum. The products of the combustion are unusually rich in sulfur dioxide.

It has been determined that this expensive treatment is unnecessary and furthermore that the acid sludge, if obtained from an oil with an asphaltic, or partially asphaltic base, may be converted almost directly into a product of commercial value.

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[1] Presented at the 57th Meeting, American Chemical Society, Buffalo, N. Y., April 2 to 7, 1919.

If samples are taken during the preliminary heating of the mixture referred to above, it may be observed when the major portion of the further refinable oil has separated. That condition obtains usually within the first hour or hour and a half, that is to say, at the end of the first stage when actual carbonization is near the minimum. Three layers form. The oil separates on top as indicated, and the excess concentrated acid accumulates at the bottom. The top layer is drawn off. The middle portion, which has not been heated high enough and long enough in contact with the concentrated acid to become carbonized and have its asphaltic nature destroyed, is a pasty mass, quite liquid at the temperature attained, and contains from 15 to 25 per cent (or even more) sulfuric acid. It is drawn off and is given one washing (1 : 5) with water. The diluted acid liquor is drawn off and sent to the concentrator. The asphaltic mass, in weighed portions, is run at once into a suitable mill, where it is mixed with the proper proportion (as determined by rapid analysis), usually in slight excess, of lime which has been freshly slaked with sufficient water to cause it to crumble into a powder. The mixture is then kneaded in the mill. Much heat is generated by the union of the free acid and calcium hydroxide, but not enough to char the material. If sufficient heat has not been generated during the mixing to render the mass fluid (due to low acid content), it may be heated to about 220° C., when as a fluid it may be run into a suitable receptacle for marketing. Finely divided limestone may be substituted for the slaked lime powder.

The asphaltic or bitumenic material present in the residuum has not been destroyed but simply incorporated with some 10 to 40 per cent of calcium sulfate, depending upon the amount of free acid present in the washed acid sludge.[1] The asphaltic or bitumenic material present may be readily extracted by the solvents generally used for dissolving those substances.

The whole mass exhibits the properties associated with asphalt, modified, of course, by the calcium salt produced. It becomes fluid when sufficiently heated and may be applied to metal, masonry, wood, etc. It adheres well and, from 6 months' test, is impervious to water. It mixes with rosin and other substances added to asphalt for particular purposes.

CONCLUSION

A by-product, formerly a nuisance, costing money to get rid of it, has been converted into a useful material possessing a commercial value.

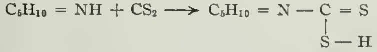
REACTIONS OF ACCELERATORS DURING VULCANIZATION[2]

By C. W. Bedford and Winfield Scott

Research Laboratories, Goodyear Tire and Rubber Company, Akron, Ohio

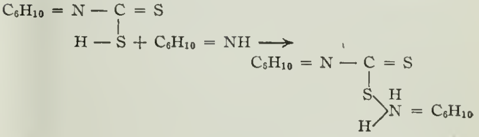
Received October 6, 1919

The highest powered organic accelerators known to-day are the carbon bisulfide reaction products of strong organic bases. Perhaps the best example is the piperidine salt of piperidyl-dithiocarbamic acid. The formation of this compound is shown by the following equations:



$$C_6H_{10}=NH + CS_2 \longrightarrow C_5H_{10}=N-\underset{\substack{|\\ S-H}}{C}=S$$

Piperidine Piperidyl-dithiocarbamic acid

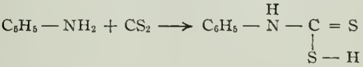


$$C_6H_{10}=N-\underset{\substack{|\\ H-S}}{C}=S + C_6H_{10}=NH \longrightarrow C_5H_{10}=N-\underset{\substack{|\\ S\diagdown\; H \\ \;\;\; \rangle N=C_6H_{10} \\ H\diagup \quad}}{C}=S$$

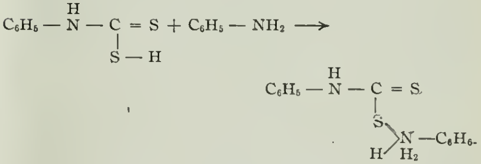
Piperidine salt of piperidyl-dithiocarbamic acid

Due to the strong basic nature of piperidine, this salt is stable and may be isolated as such. Strong aliphatic bases such as dimethylamine also give stable dithiocarbamates which are very powerful accelerators.

Thiocarbanilide, which is perhaps the most widely used commercial accelerator, is formed by the same mechanism of reaction, there first being formed the aniline salt of phenyl-dithiocarbamic acid,

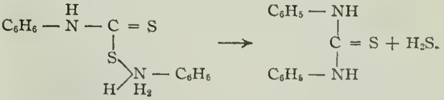


$$C_6H_5-NH_2 + CS_2 \longrightarrow C_6H_5-\overset{H}{N}-\underset{\substack{|\\ S-H}}{C}=S$$



$$C_6H_5-\overset{H}{N}-\underset{\substack{|\\ S-H}}{C}=S + C_6H_5-NH_2 \longrightarrow C_6H_5-\overset{H}{N}-\underset{\substack{|\\ S\diagdown \\ \rangle \overset{}{N}-C_6H_6. \\ H\diagup\; H_2}}{C}=S$$

This aniline salt is extremely unstable due to the weak basic properties of aniline and cannot be isolated as such. The ammonium salt of this phenyl-dithiocarbamic acid may be isolated but decomposes on standing. The metallic salts of dithiocarbamic acids are much more stable according to Krulla.[1] The aniline salt, by loss of hydrogen sulfide, produces thiocarbanilide,



$$C_6H_6-\overset{H}{N}-\underset{\substack{|\\ S\diagdown \\ \rangle N-C_6H_6 \\ H\diagup\; H_2}}{C}=S \longrightarrow \begin{matrix} C_6H_5-NH \\ | \\ C=S \\ | \\ C_6H_5-NH \end{matrix} + H_2S.$$

The stable dithiocarbamates above mentioned lose hydrogen sulfide in a similar manner when heated to the temperatures used in the vulcanization of rubber and produce thiourea derivatives. It is, therefore, quite possible that they may function as curing agents in the same manner as thiocarbanilide.

André Dubosc[2] has stated that thiourea derivatives can "furnish in a colloidal state all the sulfur necessary for vulcanization." In checking up this statement it appeared at first that Dubosc was correct, but the cures obtained were soon shown to be due to free sulfur present as an impurity in the accelerator used. Pure thiocarbanilide and pure dithiocarbamates do not vulcanize rubber in the absence of free sulfur either in a pure gum or high zinc oxide stock. We, therefore, are unable to agree with this investigator that the sulfur of such compounds is available for vulcanization.

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[1] The process is covered by U. S. Patent 1,234,985, July 1917.

[2] Presented before the Rubber Division at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

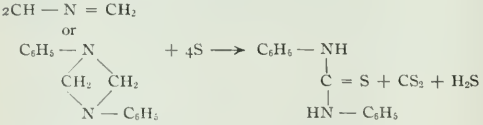
[1] *Ber.*, **46**, 2669.

[2] *India Rubber World*, February 1, 1919.

There are some dithiocarbamates which liberate the free base by a heat decomposition, such, for example, as the liberation of dimethylamine by heating its carbon bisulfide reaction product. Since these free bases are evidently good curing agents, it is possible that they may function as accelerators after being liberated by a heat decomposition of the dithiocarbamates. It is, however, not the object of this paper to discuss the mechanism of the action of thiourea derivatives as accelerators. What we wish to show is that there are many accelerators not ordinarily classed with thiocarbanilide but which undoubtedly produce thiourea derivatives by reaction with sulfur during the vulcanization process, so that they may be classed as being similar to thiocarbanilide in their ultimate action.

In June 1913, J. Bastide was granted a patent[1] wherein he claimed methylene and ethylene compounds of aliphatic and aromatic amines as vulcanization accelerators. As specific examples he mentions methylene-diphenyl-diamine and phenyl-iminomethane, the latter being otherwise known as anhydroformaldehyde-aniline or methylene-aniline. These two accelerators easily react with sulfur to form thiourea derivatives.

Methylene-aniline easily polymerizes to the di-, tri-, and probably higher polymers. We have found it convenient to consider it as the dipolymer and to take 210 as the molecular weight. It has been found that 210 g. of methylene-aniline will react with four atomic weights of sulfur, whereby one molecular weight of carbon bisulfide and one molecular weight of hydrogen sulfide are lost and that about 95 per cent of the product is thiocarbanilide. The reaction is represented by the following equations:



(I) Methylene-aniline (Dipolymer)

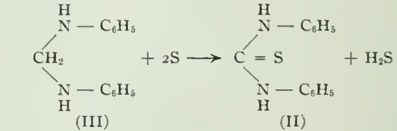
(II) Thiocarbanilide

This reaction starts at about 130° C. and proceeds best at 150° C. The amount of carbon bisulfide liberated may be determined by condensing as much as possible and weighing. Any uncondensed carbon bisulfide vapors may be caught in aniline wash bottles which have previously been saturated with hydrogen sulfide. The amount of hydrogen sulfide may be determined by absorption in caustic. A small amount of aniline and other products are formed by side reactions. It is surprising how closely the weights of the products check up with the above equation.

It is quite probable from the above data that methylene-aniline, when compounded as such, will generate carbon bisulfide during the cure. In the presence of basic amido compounds this carbon bisulfide should at once generate dithiocarbamates similar to those which have been shown by Ostromuislenskii to have such high curing power. The curing power of methylene-aniline may, therefore, be due in part to the formation of dithiocarbamates formed from carbon bisulfide liberated slowly in the cure and a subsequent reaction with amido compounds which may be present, but its chief curing power is evidently due to the direct formation of thiocarbanilide. It must not be assumed, however, that methylene-aniline should therefore have as strong a curing power as thiocarbanilide. That this is not the case is undoubtedly due to the lag of the sulfur reaction during the cure.

Methylene-diphenyl-diamine produces several reaction products when heated with sulfur, the reaction proceeding easily at 140°–150° C.

(*a*) A certain amount of thiocarbanilide is formed, as illustrated by the following equation:

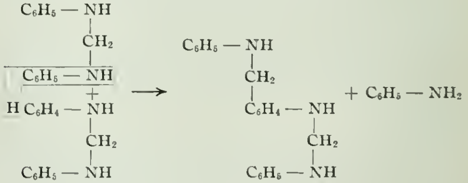


(III) Methylene-diphenyl-diamine

(II)

This reaction is desirable, but the yield is comparatively low.

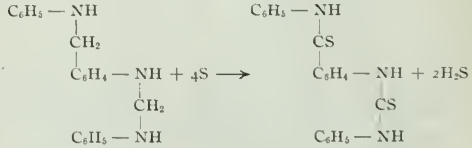
(*b*) Methylene-diphenyl-diamine by heat alone loses aniline, probably by a semidine reaction with itself.



(III)

(IV)

This reaction may be continued until the condensation has proceeded so far that one mole of the original compound has lost one mole of aniline. By reaction with sulfur before compounding and removal of such free aniline as may be formed, there is produced an accelerator of much greater curing power than the original material and which shows curing properties very similar to those of thiocarbanilide. One of the constituents of this reaction product is apparently the sulfur reaction product of Form IV.



(IV)

(IV*a*)

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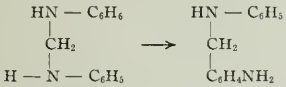
[1] French Patent 470,883.

Form IV*a* very closely resembles thiocarbanilide and is probably one of the reaction products which is formed from methylene-diphenyl-diamine when this compound is used as an accelerator for the vulcanization of rubber.

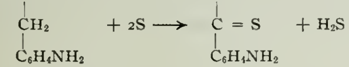
(*c*) Methylene-diphenyl-diamine in the presence of aniline, either added as such or formed by Reaction *b*, undergoes a semidine transformation with the aniline.



$$\begin{array}{c} HN-C_6H_6\\ |\\ CH_2\\ |\\ H-N-C_6H_5 \end{array} \longrightarrow \begin{array}{c} HN-C_6H_5\\ |\\ CH_2\\ |\\ C_6H_4NH_2 \end{array}$$

(III) (V)

This reaction takes place at temperatures even lower than milling temperatures. Paramido-benzyl-aniline (V) is a liquid which is crystallizable with difficulty and forms easily from (III), there being no difference in the curing power of the two compounds. Form V reacts easily with sulfur to produce paramido-thiobenzanilide.



$$\begin{array}{c} HN-C_6H_6\\ |\\ CH_2\\ |\\ C_6H_4NH_2 \end{array} + 2S \longrightarrow \begin{array}{c} HN-C_6H_5\\ |\\ C=S\\ |\\ C_6H_4NH_2 \end{array} + H_2S$$

(V) (V*a*)

Form V*a* is another compound very similar to thiocarbanilide, to which may be attributed a portion of the curing power of the original accelerator.

The main reaction of this type of methylene accelerators is evidently to substitute thiocarbonyl groups for methylene groups. This produces compounds very similar to thiocarbanilide and which may be considered as being derived from thiocarbanilide by similar condensation and semidine reactions, although we have been unable to prepare them directly from thiocarbanilide.

In the interaction of hexamethylene-tetramine with sulfur during the cure, we have another possibility of the formation of carbon bisulfide reaction products with amines. Hexamethylene-tetramine reacts very readily with sulfur at curing temperatures, producing a multitude of products including hydrogen sulfide, ammonia and carbon bisulfide in large amounts. Dubosc[1] has described the sulfur reaction products of hexamethylene-tetramine, but for some unaccountable reason has absolutely overlooked two of the main reaction products, ammonia and carbon bisulfide. The accelerating action of hexamethylene-tetramine may therefore be explained by the interaction of this ammonia and carbon bisulfide to form a dithiocarbamate. This allows us to classify hexamethylene-tetramine as a thiourea accelerator.

With a large majority of accelerators there is no possibility of the formation of thiourea derivatives by a reaction with sulfur. As far as is known, all accelerators containing methylene groups, similar to those described, react easily with sulfur at curing temperatures to produce thiourea derivatives. This does not include, however, the methylene groups of such compounds as piperidine, or pentamethylene-diamine which on heating loses ammonia and forms piperidine.

SUMMARY

I—Organic accelerators containing methylene groups, similar to those described, readily react with sulfur to produce thiourea derivatives.

II—These sulfur reactions take place at curing temperatures and may throw some light on the mechanism of the reactions of these accelerators during vulcanization.

VOLUME INCREASE OF COMPOUNDED RUBBER UNDER STRAIN[1]

By H. F. Schippel

Ames Holden McCready, Ltd., Montreal, Quebec, Canada

Received October 6, 1919

The first record of this interesting phenomenon of volume increase in rubber under strain dates back as far as 1884, when Joule recorded the fact that the specific gravity of rubber decreased upon stretching it. His test results stated a change of specific gravity of 0.15 per cent for a 100 per cent stretch. This is a very small increase, and therefore his experiments were made upon comparatively pure rubber, unmixed with pigments, as the present paper will show.

In 1889 Mallock made tests upon pigmented rubbers of different kinds, but he made the volume elasticity tests upon the samples only by applying pressure to the water in which he immersed them, thereby simply corroborating the results of the previous investigator.

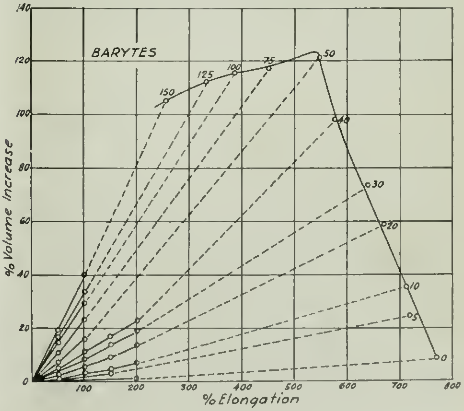


Fig. I

Again, in 1890, Sir William Thomson stated that a column of rubber when stretched out suffers no sensible change in volume, and that the contraction of any transverse diameter must be sensibly equal to $^1/_2$ of the longitudinal extension, and rubber may therefore be regarded as an incompressible elastic solid. This is also true of pure rubber.

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[1] *Loc. cit.*

[1] Presented before the Rubber Division at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 4, 1919.

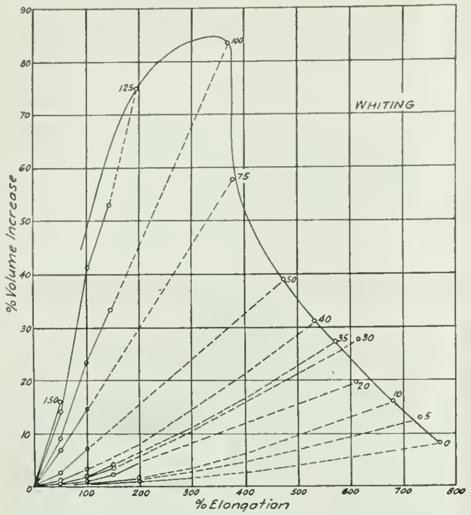

Fig. II

While studying the nature of the stress-strain curves for rubber containing different pigments in varying quantities, the writer considered the stability of the rubber surrounding each particle of pigment in the rubber body, and thought that possibly when the rubber body was elongated sufficiently the rubber might pull away from the particles of pigment in their axes of stress and cause vacua to be formed on both sides of each particle, the net result of which would be a considerable increase in the volume of the rubber body as a whole.

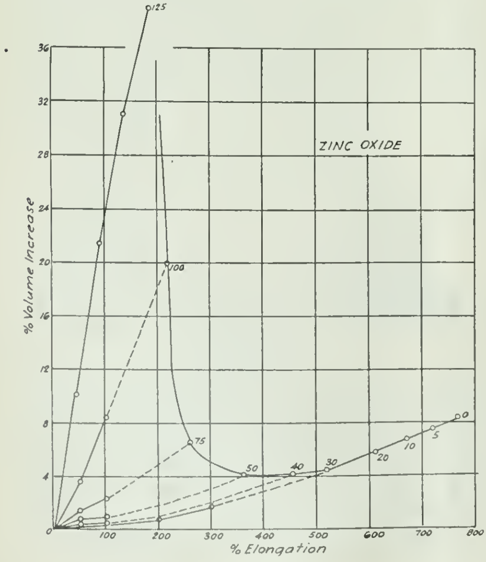

Fig. III

A preliminary test was made by preparing a transparent vulcanized compound containing a fair proportion of medium-sized lead shot. When this compound was stretched, the formation of vacua proceeded gradually until each lead shot had its conical vacua on both sides in the direction of strain. This was very satisfactory and the test was immediately applied to miscellaneous samples of rubber compounds, with the result that this integral phenomenon was actually found to take place. It was more noticeable in the red rubber than in the white. Also, after keeping the samples under tension for some time and then releasing them, temporary increases of volume were noted, which were due to sub-permanent set, or the diffusion of gases into the vacua, or both. In certain cases the observed volume increases under simple strain were remarkable. For example, a specimen made up of 100 g. fine Para, 30 g. litharge, 5 g. sulfur, and 337 g. of whiting, and press cured for 30 min. at 40 lbs. steam pressure, gave a volume increase of 52 per cent at an elongation of 140 per cent, while the estimated volume increase for a similar compound containing 215 g. barytes in place of the whiting was 120 per cent at the breaking point. In the former case, the average value of Poisson's ratio up to the breaking point was 0.39 and in the latter case 0.31. These values are not at all abnormal, but their cumulative effect in a substance which has the ability to withstand comparatively enormous elastic strains is worthy of serious consideration from a physical standpoint.

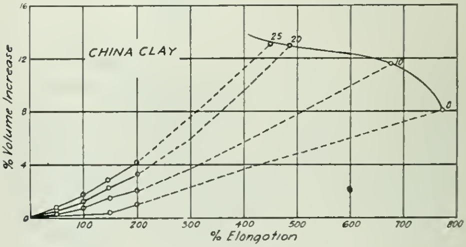

Fig. IV

For smaller percentages by volume of barytes, the volume increase was found to be less at the breaking point, and similarly for larger volume percentages, due in the latter case to the formation of local contractions corresponding to that of metals.

It was also noted that when barytes was substituted by an equal volume of lampblack the volume increases for any given elongation were smaller.

Systematic tests were accordingly made upon a series of compounds containing in various volume percentages one of the following pigments in each case: barytes, whiting, zinc oxide, china clay, red oxide, lampblack, and carbon black. The curves give graphically the results obtained.

The common base was made up of 100 parts by weight of fine Para, 5 parts sulfur, and 30 parts litharge, the weight of the test pigment added in any case being

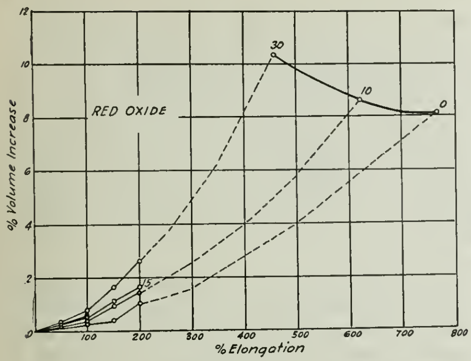

Fig. V

the volume index for that case multiplied by the specific gravity of the pigment.

A blank test was made by stretching the base only without any other pigment content. The curve obtained is marked "O" on each series of curves for the pigments.

METHOD OF PROCEDURE

Test rings, having a cross-sectional diameter of $^1/_2$ in., and an outside diameter of $2^1/_4$ in., were made from each compound up to about 35 volumes content. For volumes above this, the compounds were too stiff to make a perfect fit in the ring mold, and flat slabs about 100 mils thick were made, from which flat rings were cut. The internal circumference of the rings was approximately 4 in. Each ring was stretched consecutively over each of a graduated series of steel bars from 3 to 8 in. long, or as far as the ultimate stretch of the rubber would allow, and the volume increase was calculated by determining the change of specific gravity. This method, which avoided the construction of any special apparatus, and was very accurate, was the suggestion of Mr. W. B. Wiegand, whose inspiring coöperation in this and other rubber researches the writer takes pleasure in acknowledging.

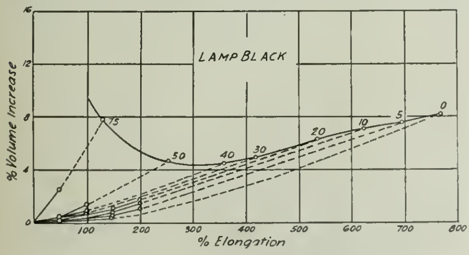

Fig. VI

(I) BARYTES—The test results are shown by that part of each curve in full line. It was found impossible to obtain higher elongations than 200 per cent for the large rings, owing to their failure by slow tearing when stretched above this value. The curves approximate closely to straight lines, showing that the volume increase varies almost directly with the elongation. Also, for a constant elongation, the volume increase progresses with the percentage of barytes in a roughly proportionate manner. There appears to be no adhesion whatever (or very little) between the rubber and the particles of barytes, because there is a volume increase in the compound containing only 5 volumes of barytes. The particles are certainly not crowded in a 5 per cent mix, and their surfaces do not necessarily transmit the whole local stress, but on account of this early separation of the pigment particles from the rubber, the particles take no important part in the stress-strain curve for the body, since the stress is transmitted through the rubber only.

It was thought that possibly the large volume increases might be due to the pigment entering the rubber in agglomerated masses, and that most of the increase in volume might be due to ready separation of particles which were in dry contact. Accordingly, two tests were made to determine this, one test of a sample of compound milled for 60 min. instead of 21 min. for the normal mix, and another test upon a sample which was softened to cement consistency in gasoline, thoroughly mixed, dried, and press-cured as usual. The excessively milled sample showed a very slight decrease of percentage volume increase, but the decrease of this property in the cement sample was more considerable. The entry of the gasoline into the compound presumably softened the rubber and allowed it to flow around each particle, wetting the whole mass of pigment thoroughly; so that, although part of the volume increase under stretch is due to the separation of pigment surfaces in dry contact, the larger part of the increase is due to rubber separation from the surface of the particles.

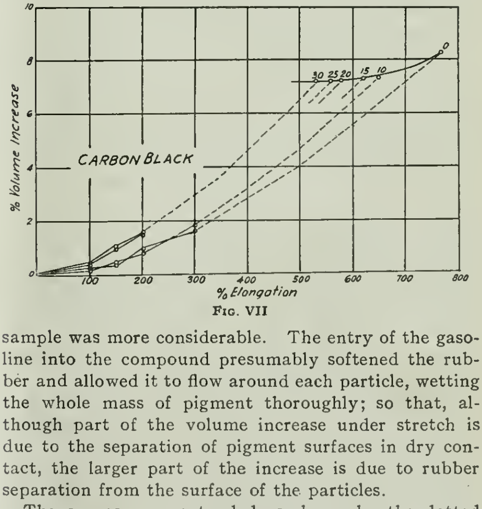

Fig. VII

The curves were extended as shown by the dotted lines to the point corresponding to the ultimate percentage elongation as obtained from standard breaking tests on a tensile testing machine. The full-line curve joining these points is of special interest. The discontinuity above 50 volumes is due to the formation of local contractions in the test ring, so that the whole body of rubber does not receive the same proportional elongation. The neck is similar to that formed on metal specimens. By mechanically working the rubber rings until the stiffness is removed, greater volume increases are obtained, *i. e.*, we obtain points on the true extension of these curves. In the same way higher elongations could be obtained on the tensile testing machine.

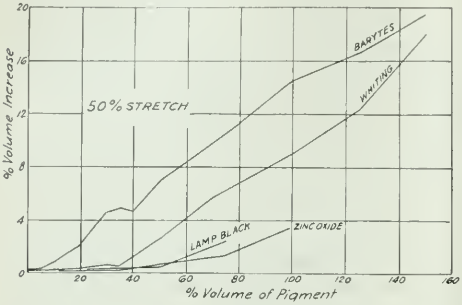

Fig. VIII

(II) whiting—The curves for this series of compounds show that up to 40 volumes of whiting the percentage increase is comparatively small, then there is a sudden jump in volume increase with further addition of pigment, until at 150 volumes the whiting gives almost equal results to barytes. This probably is due to agglomeration of the pigment particles when present in large amounts. It should be noted that these curves are plotted on a more open scale of per cent-volume increase than that of the barytes.

(III) zinc oxide—The trend of the zinc oxide curves up to 30 volumes is identical with that of the basic mix, although the ultimate elongation is reduced as much as 250 per cent. This shows that there is a strong adhesion of the rubber to the particles of zinc oxide, which imparts additional strength to the basic mix, but which reduces the ultimate elongation on account of the dilution of the rubber. This phenomenon classifies zinc oxide physically with the finer pigments, lampblack and carbon black. The upward shift of the curves for volumes above 30 indicates a rapid growth of agglomerated masses of particles which greatly reduces the tensile strength of these compounds. The shape of the almost complete 125-volume curve indicates that the large extrapolations of the other curves are approximately correct.

(IV) china clay—The range of volumes experimented upon is not so large, but there is indicated an increase in volume for the low percentages of pigment. The open scale of "volume increase" to which these curves are plotted should be noted. The trend of these low volume curves away from the basic mix curves shows that the addition of china clay to rubber lowers the tensile strength in the compounds.

(V) red oxide—The red oxide, being a finer pigment than china clay, shows less volume increase under strain. Also, departure from the curve of the basic mix shows a weakening effect upon the compound.

(VI) lampblack—The volume increase of the lampblack compounds is graduated proportionally to the content of lampblack up to 50 volumes. The 75-volume compound shows a considerable rise of volume increase, which indicates a rapidly increasing agglomeration of the particles. This means that the limit of ability of the rubber to wet each particle of lampblack has been reached at 50 volumes, and above this volume the rubber surrounds groups of particles, instead of embedding each particle individually.

(VII) carbon black—A 30-volume content of carbon black lowers the ultimate elongation of the rubber to 530 per cent, while the same volume of lampblack lowers it to 420 per cent. This indicates a greater weakening effect of the lampblack on the rubber, although the volume increase under equal strain is less.

curves for 50 per cent and 100 per cent stretch—Figs. VIII and IX show the property of volume increase in a different light. Here the variation of percentage volume increase is shown on a "volume of pigment" base for constant elongations of 50 per cent and 100 per cent. These curves are really a more distinct representation of the growth of agglomerated masses of pigment as the volume of pigment is increased. It will be noticed that at 100 per cent stretch the whiting and zinc oxide curves tend to approach the barytes curve, due to the more rapid formation of agglomerated masses of these pigments than of those of the barytes. Since the average particle of whiting has only one-eighth the volume of the average particle of barytes, it would require an agglomeration of the whole body of whiting into average groups of eight particles each to cause the whiting curve to meet the barytes curve, or multiples of eight, if there already existed an agglomeration of the barytes particles. This agglomeration of the pigment particles and the phenomena connected with it are of vital importance, since the sudden growth of agglomerated particles at certain volumes may be coincident with a rapid in-

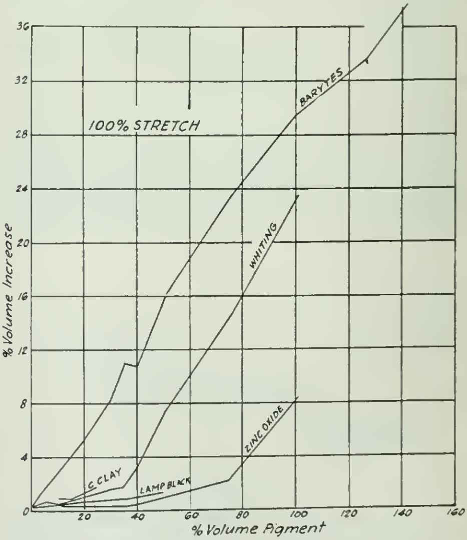

Fig. IX

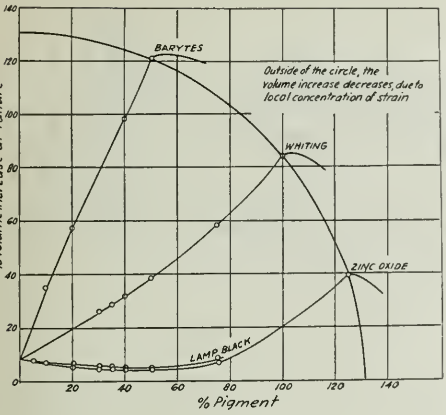

Fig. X

crease of hysteresis, due to the friction when the rubber body is distorted, among those particles which are in dry contact with each other. Conversely, any means of reducing the agglomeration of pigment should also be the means of reducing the hysteresis, such as the method of milling, and the use of solvents to reduce the viscosity of the rubber while mixing in the pigment.

Fig. X shows the percentage volume increase at failure on a base of percentage pigment, plotted up to the point of maximum volume increase, which takes place, as mentioned before, when local contraction of area occurs. These maximum points, as shown for the three pigments, barytes, whiting, and zinc oxide, lie approximately on a circle having the origin as center. The lampblack curve cannot be extended sufficiently far to reach the maximum volume increase due to the inability of the rubber to absorb large quantities of lampblack. The curves for china clay, red oxide, and carbon black are not shown, but as far as they have been obtained, they fall between whiting and zinc oxide, the china clay lying highest and the carbon black lowest of the three.

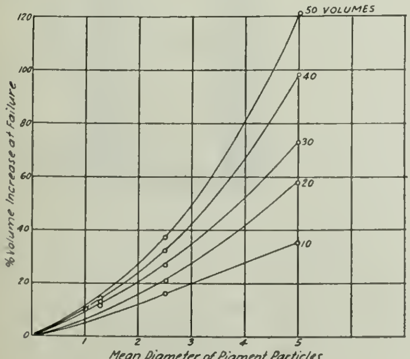

Fig. XI

Fig. XI undoubtedly shows the real explanation of the variability of the pigments from the volume increase standpoint. They show that, with the exception of zinc oxide, the greater the mean diameter of the pigment particles, the greater is the volume increase under strain. A confirmation of this statement was the result of a test on four samples of barytes compounds containing equal volumes of barytes of different degrees of fineness. The different grades were prepared by allutriation in water. The compound containing the finest grade of barytes showed the least volume increase under strain. This was a critical test which eliminated every other variable but the size of the pigment.

THE EXPANSION OF RUBBER COMPOUNDS DURING VULCANIZATION[1]

By C. W. Sanderson
Fisk Rubber Company, Chicopee Falls, Mass.

Received October 29, 1919

The extent to which rubber compounds will expand when subjected to the heat of vulcanization is of importance in the molding of rubber goods. As far as published results go, however, there are no available data on the value of the coefficient of expansion of rubbers of different compositions.

The work was undertaken by us primarily from a practical point of view, with the object of determining whether or not use could be made of an expansion test in distinguishing between stocks which move freely and mold well and those which do not mold well and are characterized as being "dead." Other possibilities suggested themselves and although the results are by no means complete or beyond question, they are set forth as we have found them.

APPARATUS

A special apparatus was designed for the investigation (Fig. 1). It consists of a hollow steel cylinder which may be filled with rubber and which is surrounded by a steam-jacket. The top surface of the rubber is the only surface free to move when the rubber is heated, and it acts against a piston and spring. The motion is transmitted through a magnifying lever to a recording pencil. The piston, spring and recording mechanism were taken from a Crosby steam indicator gauge and made over to fit the apparatus. Above the piston is a place for a spring to keep pressure enough on the rubber so that it will not "blow." Ten-, 50- and 100-pound springs were used. The 10-pound spring was hardly strong enough to prevent blowing. The use of the 50- and 100-pound springs will be mentioned later.

In making the determinations of the expansion the rubber was heated at a constant rate, usually 20° per 5 min. The recording cylinder was advanced at each interval and from the values on this graph smooth curves could be drawn.

The dimensions of the steel cylinder were:

Diameter, 0.7978 in.
Height, 2.0 in.

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[1] Paper presented before the Rubber Division at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

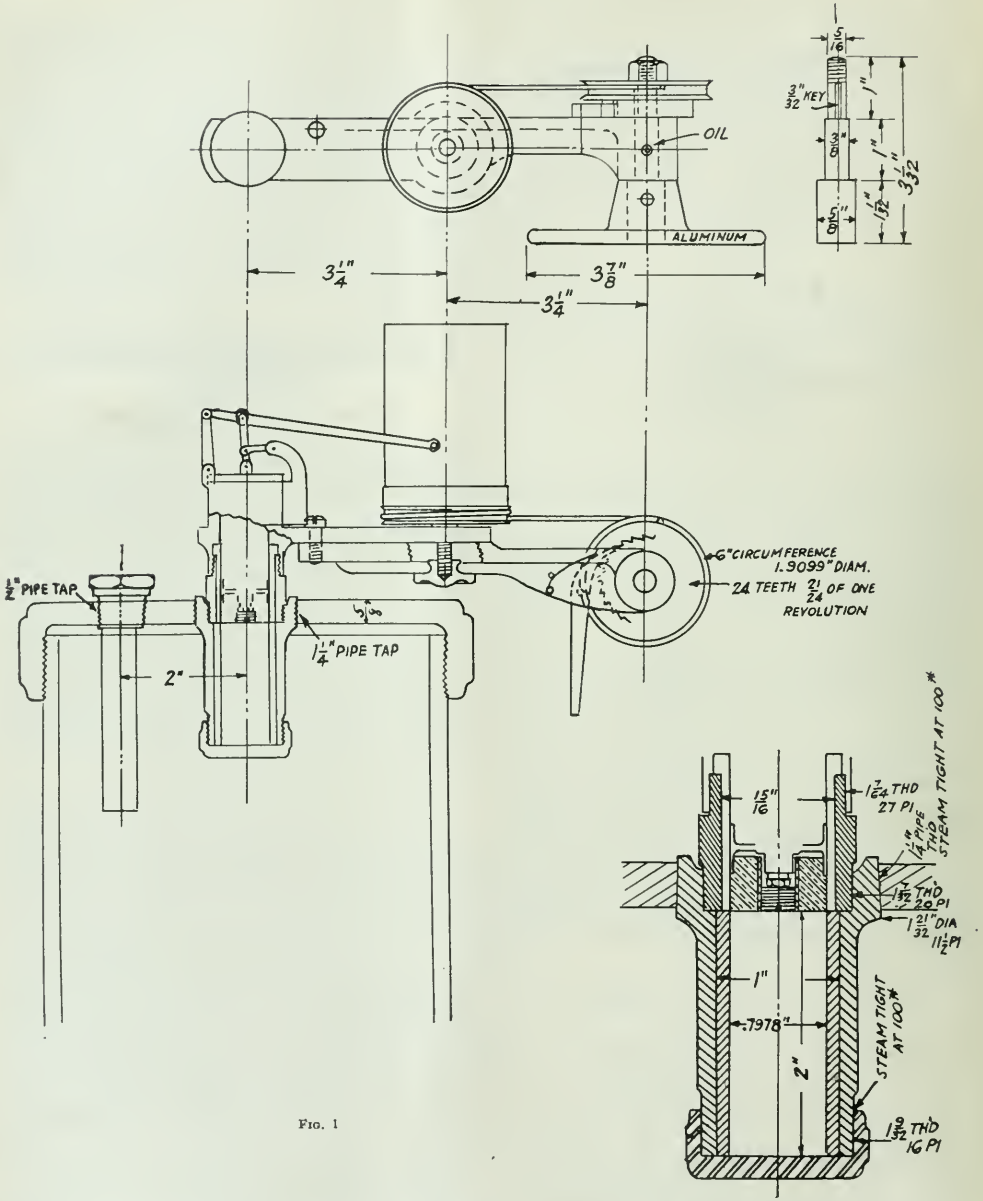

Fig. 1

These dimensions were chosen so that at room temperature (80° F.) the volume of the contained rubber was one cubic inch. The motion of the recording pencil was reduced to the motion of the piston by dividing by six.

The cubical coefficient of expansion was derived from the regular forms.

$$a = \frac{V_t - V_o}{V_o\, t} \text{ and } V_t = V_o\,(1 + a\,t)$$

and worked out as follows:

$$a = \frac{\left\{[0.3989\,(1 + 0.0000061\,t)]^2 \times 3.1416 \times \left(2 + \frac{x}{6}\right)\right\} - 1}{1 \times t}$$

where t = Temperature change
x = Expansion recorded on the chart

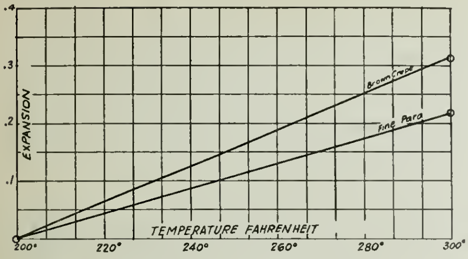

FIG. 2—CURVE SHOWING EFFECT OF RUBBER ON RATE OF EXPANSION 1698 FINE PARA *vs.* 1698 BROWN CREPE

This reduces to

$$a = \frac{(0.3989 + 0.0000024\,t)^2\,(6.2832 + 0.5236x) - 1}{t}$$

If we neglect the expansion of the steel shell and approximate, the formula may be reduced to a much simpler form:

$$a = \frac{x}{12\,t}$$

It was found that the differences in the results obtained with the exact and with the approximate formula were less than the experimental errors. The approximate formula was therefore used in our work.

VALUE OF THE COEFFICIENT

No.	USE	Coeff.[1]	Rubber by Vol. Per cent	Specific Gravity Raw	Specific Gravity Cured
1.....	Tube	4.680×10^{-4}	90	0.89	0.96
2.....	Tube	4.023×10^{-4}	94	0.95	0.95
3.....	Pneumatic Tread	3.365×10^{-4}	70	1.18	1.23
4.....	Semi-Hard	3.322×10^{-4}	48	1.41	1.47
5.....	Pneumatic Tread	3.000×10^{-4}	66	1.39	1.40
6.....	Sidewall	2.807×10^{-4}	66	1.50	1.53
7.....	Solid Tire	2.828×10^{-4}	71	1.83	1.87
8.....	Pneumatic Tread	2.73×10^{-4}	59	1.44	1.53
9.....	Hard Rubber	1.121×10^{-4}	58	1.31	1.33

[1] Steel, 1.83×10^{-6}; Ebonite (Smithsonian table), 4.6×10^{-5}.

In general the results show that the higher the rubber content, the higher the coefficient of expansion. It is, however, difficult to show any definite relation because, as will be shown later, other factors enter in.

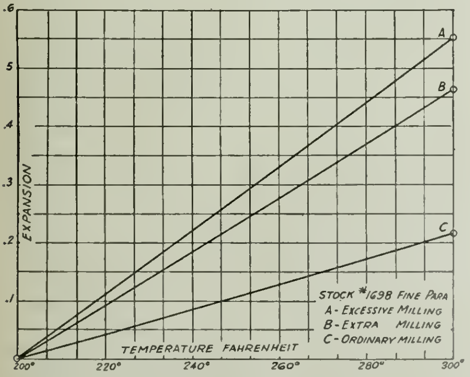

FIG. 3—CURVE SHOWING EFFECT OF MILLING ON RATE OF EXPANSION

NATURE OF THE EXPANSION

The graphs obtained showed that after the first 15 min. the expansion curve was practically a straight line. The beginning of its curve showed a lower slope because of the fact that the rubber was not thoroughly heated through or perhaps had not been put in so as entirely to fill its cavity. Therefore, all measurements taken to determine the value of the coefficient were taken over the range of 200° to 300°. Some of the lower grade compounds, especially those with high sulfur contents, showed a lessening of the slope and even a falling off in the curve after 300° had been reached.

INFLUENCE OF THE RUBBER

Two samples were made up from the same formula, using in one fine hard Para and in the other a soft grade of brown crepe (Fig. 2). Each was subjected as nearly as possible to the same amount of milling. The Para sample gave a coefficient of 2.337×10^{-4}, while the brown crepe gave 4.49×10^{-4}.

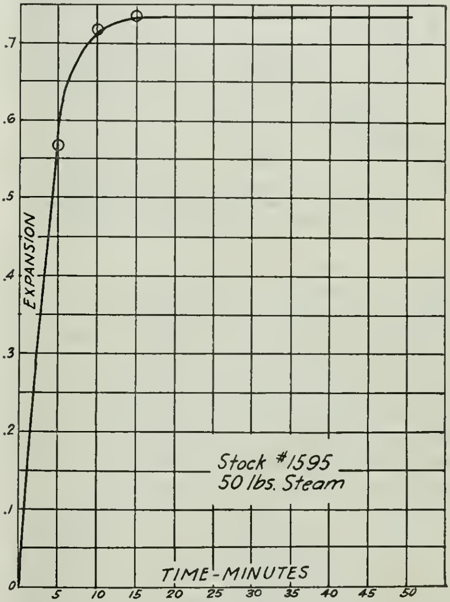

FIG. 4—CURVE SHOWING EXPANSION AT CONSTANT TEMPERATURE

INFLUENCE OF MILLING

Other parts of the same batch with the Para rubber were subjected to further milling and a sample gave a coefficient of 4.680×10^{-4}, while another sample which had been milled to excess on hot rolls gave a value of 4.786×10^{-4} (Fig. 3). Then it is seen that milling increases the expansion and brings the value for Para up to that for the brown crepe.

VOLUME CHANGE AT CONSTANT TEMPERATURE

One of the first questions which arose in connection with the expansion of the rubber was whether or not there was a break in the curve or, in other words, a volume change at the point of vulcanization. We know that a physical change takes place and that the specific gravity increases and therefore it was only natural to look for a drop in the expansion. The curves obtained with a rising temperature failed to show any drop so samples were tried using a constant temperature or, in other words, subjecting the sample to the same condition as an ordinary cure (Fig. 4). The graphs failed to show any drop with the exception of the cases already mentioned. Even in those cases the drop was very gradual and did not start at the point of vulcanization. Therefore, the method could not be used as a method of regulating or determining the cure of a sample of rubber.

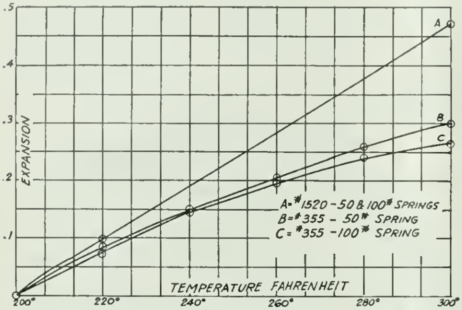

FIG. 5—CURVE SHOWING EFFECT OF DIFFERENT PRESSURES ON TWO RUBBERS, ONE OF WHICH SHOWS A LARGE AND THE OTHER A SMALL DIFFERENCE BETWEEN RAW AND CURED SPECIFIC GRAVITIES

Since the curves failed to show any volume contraction during the heating process, the increase in specific gravity which always occurs must come as the result of the pressure and the subsequent contraction on cooling. Since rubber is nearly incompressible, the decrease must come as the result of the squeezing of air out of the raw rubber. If this be true, then a compound showing a big difference between raw and cured specific gravity will expand more against a light spring than against a strong one. This was tried out and found to be the case (Fig. 5).

STOCK	EXPANSION AGAINST SPRING	
	50 lb.	100 lb.
1520	3.81×10^{-4}	3.81×10^{-4}
355	2.17×10^{-4}	1.36×10^{-4}

SPECIFIC GRAVITIES

STOCK	RAW	CURED IN HYDRAULIC PRESS	CURED IN EXP. APPARATUS	
			50-lb. spring	100-lb. spring
1520	0.95	0.957	0.956	0.956
355	1.457	1.568	1.568	1.577

EXPANSION *vs.* CONTRACTION

The increase in specific gravity shows that the contraction is greater than the expansion. Therefore the question arises whether or not the values obtained apply to the cured rubber. In order to determine this, measurements were made on samples cured in a disc mold.

Aluminum mold	No. 6 Sidewall
Diameter of mold, hot	$3\frac{31}{32}$ in.
Diameter of rubber, cold	$3\frac{29}{32}$ in.

$$a = \frac{L_t - L_o}{L_o\, t} = \frac{0.0625}{39063\ (218)}$$

$$a = 0.00007339$$

$$a \text{ (cubical)} = 2.20 \times 10^{-4}$$

This compares with 2.8×10^{-4} obtained the other way. This is a check considering the fact that the rubber was of a different sample and was from mill stock, while the expansiometer sample was from calendered stock. The conclusion may be drawn then that the coefficient determined between 200° and 300° may be taken as sufficiently accurate for the coefficient for vulcanized rubber from the same sample.

CONCLUSIONS

Although it is not yet possible from the results obtained with this apparatus to state definitely whether or not a stock will mold well in factory practice, it does give us a means of distinguishing between batches of the same stock which may have different properties, due either to rubber, milling, or other conditions.

The results may be summarized as follows:

I—The values of the coefficient of cubical expansion for different grades of rubber have been determined.

II—The higher the rubber content the greater the expansion.

III—The harder the crude rubber the less the expansion.

IV—The more the rubber is milled the greater the expansion.

V—There is no break in the expansion at the point of vulcanization.

VI—The increase in the specific gravity is caused by the pressure and not by physical change or internal contraction of volume.

THE MOISTURE CONTENT OF CEREALS

By O. A. Nelson and G. A. Hulett

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Received July 29, 1919

The determination of the moisture content in colloidal organic substances presents peculiar difficulties, as has been pointed out in previous work on the moisture content of coals.[1]

The layer of water adsorbed on the surface of colloids has quite different properties from that of ordinary water. Its vapor pressure is much lower, and if this layer is of molecular dimensions it cannot be removed by the best dehydrating agents in a vacuum desiccator.[2] In order to get an idea of the situation, consider a cubic centimeter of the organic materials that go to make up coals, plant materials, cereals, etc., divided into little cubes 10^{-6} cm. on each edge. The area of the faces of these little cubes would be 600 sq. m. If these surfaces were covered with a layer of water approximately 1×10^{-8} cm. thick, there would be 0.06 cc. of water, or over 5 per cent of the weight of the substance, and this water would be in a condensed condition so that it would show practically no vapor pressure. If the layer were one-tenth the thickness of the assumed cubes, it would make up 50 per cent of the weight, and still the vapor pressure would be less than that of normal water, so the substance would take up moisture from moist air and still feel "dry." Such is the case of peat containing as much as 75 per cent water.[1]

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[1] E. Mack and G. A. Hulett, *Am. J. Sci.*, **43** (1917), 89, and **45** (1918), 174.

[2] *Loc. cit.*, p. 92.

Colloidal substances containing a large amount of moisture readily give up water to dehydrating agents or when heated in an air bath to 105°–110° C., but due to the fact that the vapor pressure continually drops with the removal of successive layers of water the system soon reaches such a low vapor pressure that a measurable amount of water is no longer obtained, even though considerable moisture is still present.

Attempts have been made to remove the water by chemical means, *e. g.*, by mixing the substance with calcium carbide and measuring the acetylene formed.[2] This method is not applicable in all cases and has not found very much favor. The majority of methods are based upon the increasing vapor pressure of the water by raising the temperature, and depending on evaporation or dehydrating agents for its removal. But with organic substances one is limited as to temperature on account of chemical decompositions which form water.

Heating in an air bath or in an atmosphere of indifferent gas to a temperature of 105°–110° C. is the common practice for moisture determinations, and gives a useful commercial test method, but does not give the true moisture contents. In the case of coals, *e. g.*, it was found that the true moisture contents were from 30 per cent to 50 per cent greater than that given by the official "moisture" method. It was also found possible to heat coals in a vacuum to above 250° C. (in many cases to 300° C.) without appreciable amounts of decomposition. But in the case of coals the cellular structure of the original material all disappeared in the early stages of decomposition and, also in the long process of forming coals the more decomposable matters have presumably disappeared. So we are dealing with a comparatively favorable substance. In the case of cereals and natural organic substances which have their cellular structure and contain easily decomposable matter, the problem of determining the moisture which is present as such is obviously a far more difficult one than for coals.

Generally organic substances decompose non-reversibly, giving gases, *e. g.*, CO_2, CO, CH_4, H_2, moisture, and a residue, and we have reason to believe that there is no definite temperature of decomposition such as a boiling point or a freezing point, but that we are dealing with chemical reactions which go on at *all* temperatures, but with widely different rates. A substance that decomposes readily at 200° or 300° C. also decomposes at lower temperatures, but often so slowly that no measurable results are obtained in experimental time.

When an organic substance with water as its external phase is heated in a vacuum, water is given off. If this water is removed as fast as it is liberated at a constant temperature, the rate of removal is fast at first, then falls off rapidly and in time entirely ceases. If we plot the per cent of moisture against time we get a curve like the 105° C. curve of Fig. 1. Now if the experiment is carried out at a higher temperature, another curve is obtained lying just above the one considered. The reason for the relative positions of these curves may readily be understood from the viewpoint of the lowering of the vapor pressure due to thinner and thinner layers of water as outlined above.

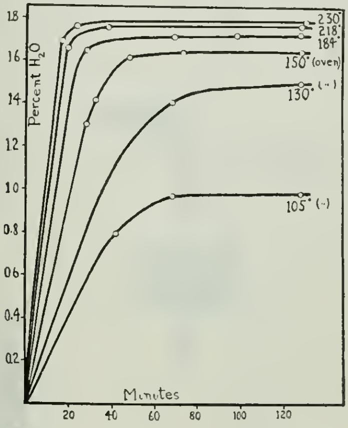

Fig. 1

When the curve runs parallel to the time axis it means that no more water is being liberated at that particular temperature. Water may still be present but with such a low vapor pressure that sensible amounts do not leave the substance in experimental time, although at a higher temperature with increased vapor pressure more water is obtained and continues to be liberated until the vapor pressure again drops, and in time the curve runs parallel to the time axis. When, however, we reach a temperature at which the rate of decomposition is rapid enough to furnish measurable amounts of water, the flat part of the curve will not be parallel to the time axis, but will gradually rise. Such a series of curves gives us information as to the temperature and time we may heat the substance in question without encountering measurable amounts of water arising from decomposition of the material.

METHOD AND APPARATUS

The apparatus used was a modification of the one used in previous work[1] on coals and is represented diagrammatically in Fig. 2. Glass tube A was about 200 mm. long and 12 mm. in diameter, fitted with a ground stopper having a capillary side tube containing the stopcock S. Glass tube B was closed at both ends and fitted inside of A for the purpose of reducing the "dead space" of the system. The boiler C contained the constant boiling liquid. D was an electric heater, and E was a condenser made of thin glass, about 80 mm. long, with a diameter of 7 mm. Solid carbon dioxide, F, was used for the purpose of maintaining a temperature of —78° C. It was found

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[1] *Am. J. Sci.*, **43**, 89.

[2] H. C. McNeil, Bureau of Chemistry, *Bulletin* **122** (1912).

[1] *Loc. cit.*

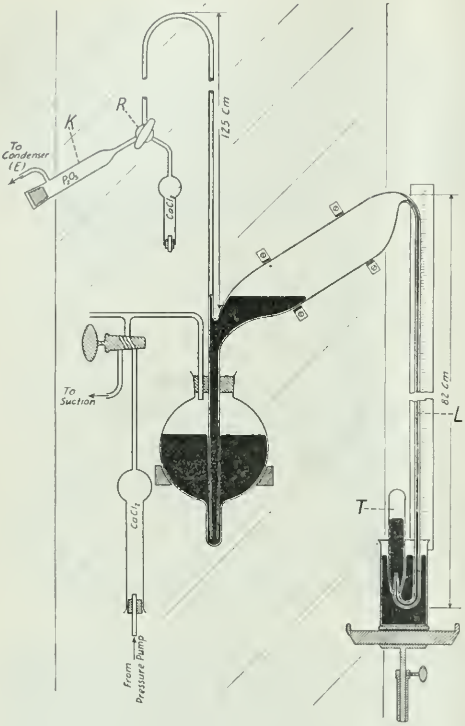

Fig. 2

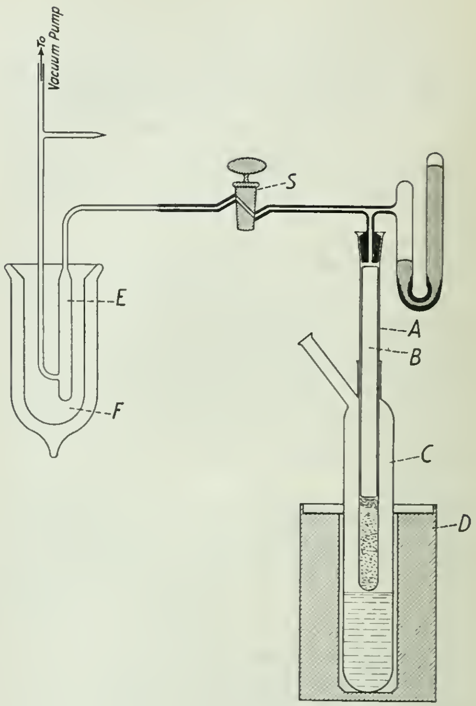

Fig. 2a

quite possible to weigh tube A in the balance, so the sample to be used was weighed directly. In case the sample was a fine powder a wad of glass wool was placed on top before tube B was adjusted, as it was found that without this some of the substance would pass along with the gases when stopcock S was opened to a vacuum. After the condenser E had been sealed in place the system was evacuated as far as the stopcock S, and the condenser warmed in order to remove any moisture that might be adsorbed on its inner surface. This water was taken up by the P_2O_5, in K. After the condenser had been cooled to —78° C. the stopcock S was opened, and the air, adsorbed gases, and moisture passed rapidly out of A. The moisture was condensed as *ice* in tube E while the gases passed on and were collected in T and reserved for analysis. This modification of the original "coal apparatus" made it possible to make determinations of the moisture liberated at any stage of the experiment, since it was an easy matter to close stopcocks S and R, cut out the condenser and seal on another, without interrupting the heating, an operation that required only 10 or 15 min.

The vapor baths which we used to obtain constant and reproducible temperatures were: water for 100° C.; pyridine for 115° C.; chlorbenzene for 132° C.; xylene for 142° C.; brombenzene for 155° C.; aniline for 184° C.; naphthalene for 218° C.; and *p*-mononitrotoluene for 237° C.

Since we were using a Töpler pump and toward the end of the experiment had a very high vacuum (less than 0.0001 mm. above the vapor pressure of mercury at room temperature), it became a question whether all the moisture was retained in E, or whether some was carried over into the P_2O_5 tube, K. This was tested in the following ways: Two condensers, E, were sealed together in series and sealed in place in the system. The one next to A was left empty while 0.1472 g. of water was weighed into the second. A moisture determination was then made on a sample of wheat flour, and after heating and evacuation the required length of time (4 to 5 hrs.), the amount of water in each condenser was weighed separately. The water remaining in the second tube weighed 0.1472 g., exactly the amount that had been weighed into it, thus indicating that either no water had escaped or that this amount was the same as that which had come over from the first condenser. In order to make sure that the second possibility was not the true one the following test was made: A small amount of water was weighed into a condenser, E, but instead of sealing it to A it was guarded by a P_2O_5 tube with a stopcock, and evacuated. Then 10 or 15 cc. of air were allowed to pass slowly (during 4 or 5 hrs.) through the P_2O_5 tube over the "ice" and collected in T. The weight of the water filled into the condenser originally was 0.1887 g. and at the end of the experiment the water left in the tube weighed 0.1886 g. This indicated that all the water had been retained in E. Our Töpler pump, fitted with a calibrated fall tube, served also as a McLeod gauge, and we have calculated that the pressure in the system was often less than 0.0001 mm. Water at —78° C. has a vapor pressure of 0.0005 mm.[1] and we feared a loss, but evidently the rate of evaporation at these low pressures, 0.0005 mm. to 0.0001 mm. or less, is so slow that not a measurable amount is lost in experimental time.

The method as now employed permitted us to pump the moisture and gases from the samples at any given temperature, retain the moisture in E as ice, and collect and measure the gases. Furthermore, the small amounts of gases liberated, on continued heating at a given temperature, were measured in the fall tube L and it was possible to measure the minutest traces with high precision. It was exactly this part of the gas-time curve that was important.[2] As already pointed out, we are concerned with the moisture-time curve when heating at a given temperature, but we have found that gases are also given off with adsorbed water, and a series of gas-time curves have the same character as the moisture-time curves of Fig. 1. It was an easy matter to follow the gases liberated with time. Furthermore, when organic substances decompose to form water, gases are also formed and generally in more noticeable amounts than water. So this method is a particularly sensitive one for determining decomposition.

As mentioned above, the moisture liberated during a run was condensed as ice in E. Ice does not dissolve gases, so aside from moisture only vapors which have a pressure of the order of water at —78° C. would be retained. The tube E was cut out, wiped and weighed carefully, and the water removed and examined. It was then dried inside by blowing dry air through, and again weighed, thus the total amount of water liberated during the run was directly and accurately determined. We removed and replaced E with a fresh tube at intervals during the experiment, and thus the total amount of water was "analyzed" as to rate of liberation.

We may now take the total amount of water liberated in each run and plot against the corresponding temperatures and get moisture-temperature curves which show distinct breaks (Fig. 3).

If we evacuated a sample and measured the liberation of moisture and gases with increasing temperatures, the results gave little information, for the liberation of moisture and gases was so slow that no characteristic points appeared. In fact it was found necessary to maintain the temperature from 3 to 6 hrs. to find out all that would happen at that given temperature.

The moisture-temperature curves indicate to us the amount of moisture liberated at each temperature, and the break shows the point of temperature at which deposition becomes measurable when the sample is heated for 3 hrs. or more. It does not necessarily show the total amount of moisture that is actually present in the substance but it does show the time and temperature to which we may safely heat the substance. By extrapolating the flat part of the curves beyond the breaks we may get an idea of the total amount of moisture present as such.

In addition to determining the moisture contents of wheat flours and corn meal we have also made moisture determinations on cornstarch, celluloses and one protein (Edestin). Since these substances are the main constituents of the greater number of cereals it was of importance to know not only the moisture contents of each but more so to know the temperature at which decomposition became rapid. Some of the results of our experiments are given in the tables.

SAMPLE	Temp. Deg. C.	Per cent Water	Vol. Gas per G. of Sample Cc.	Time Sample Heated	
				Hrs.	Min.
Wheat Flour (P. C. 20094)..	100	10.80	0.007	4	00
	115	10.87	0.017	6	20
	132	10.98	0.030	5	00
	142	11.01	0.077	6	20
	155	11.12	0.125	6	00
	184	11.41	0.400	4	00
	218	13.37	2.762	3	20
Corn Meal (P. C. 20093)....	100	11.34	0.000	4	40
	115	11.37	0.042	6	45
	132	11.70	0.172	6	00
	142	11.93	0.231	6	15
	155	12.12	0.402	4	00
	184	12.17	0.421	4	30
	218	12.32	2.188	2	00
Corn Starch (S–1)..........	100	11.80	0.000	4	40
	115	12.09	0.001	4	00
	132	12.16	0.017	4	00
	142	12.27	0.031	4	45
	115	12.30	0.124	4	00
	184	12.32	0.685	3	00
	218	12.46	2.423	1	00
Cellulose (Swedish Filter Paper)....................	115	2.63	0.001	3	30
	132	2.67	0.037	4	10
	155	2.71	0.098	4	20
	184	2.72	0.234	3	45
	218	2.93	0.572	2	00
	237	3.61	1.269	2	00
Cellulose (Absorbent Cotton)	115	5.49	0.000	2	00
	132	5.55	0.010	3	00
	155	5.57	0.018	3	00
	184	5.63	0.058	5	00
	218	5.74	0.070	3	00
	238	6.11	0.321	2	40
Protein (Edestin)...........	100	10.40	0.000	2	00
	115	10.63	0.010	2	15
	132	10.82	0.018	2	00
	156	11.08	0.057	3	10
	184	11.67	0.153	3	45
	218	14.06	1.845	3	00

DISCUSSION OF RESULTS

One point of importance to be noted about the moisture-temperature curves, Fig. 3, is that none show any distinct breaks before a temperature of 184° C. is reached and, with the exception of wheat flour and protein, the deviation from a straight line is very slight until 218° C. is reached. This means that with these two exceptions the water arising from decomposition while heating for over 3 hrs. in a vacuum is very slight even at this high temperature. Proteins and substances containing large amounts of these compounds decompose at temperatures somewhat lower than do starches and celluloses, a thing that would probably be expected if we consider the very complex structure of the molecules that go to make up these substances.

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[1] Dushman, *Phys. Rev.*, **5**, 223.

[2] In measuring these small amounts of gas in the fall tube, the Töpler pump must be free from all traces of moisture, so the P_2O_5 in tube K must be kept in first-class condition.

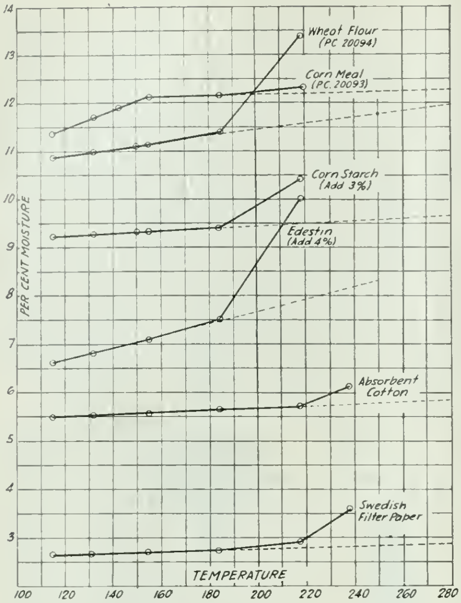

Fig 3

As has been pointed out above, these results do not represent the true moisture contents of the substances tested. To obtain these we have to extrapolate the flat part of these curves to some higher temperature. Here, however, we are confronted with the question as to what temperature we needed in order that no water may remain as adsorbed water in the substance. Obviously it is impossible to determine this by direct experiment, because most of the substances found in cereals decompose readily when we get much above 200° C. In the case of coals it was found quite safe to use temperatures as high as 300° C. without encountering appreciable amounts of water due to decomposition, and also that at this temperature probably all the moisture was given off. Considered from another point of view, we have reason to believe that very little water can be retained in an adsorbed and colloidal state at this temperature. We know that above 365° C. (the critical temperature of water) water cannot exist as a liquid, no matter how much pressure is applied, from which we may infer that at these high temperatures, where water is incapable of existing except as a gas, colloidal and adsorbed water should be removed much below this temperature in a high vacuum. With substances where the flat part of the curve rises rapidly with temperature it is quite safe to assume that there cannot be any adsorbed water at 250° C. The true moisture contents of the substances tested would therefore be as follows:

Substance	Per cent Moisture
Wheat Flour (P. C. 20094)	11.8
Corn Meal (P. C. 20093)	12.25
Corn Starch (S–1)	12.4
Protein (Edestin)	12.3
Cellulose (Swedish Filter Paper)	2.8
Cellulose (Absorbent Cotton)	5.9

The gas-temperature curves (Fig. 4) show very nicely at what temperature decomposition becomes rapid. It is to be noted that there are no very sharp breaks in any of these curves, which is in accordance with the assumption that there are no definite temperatures of decomposition. However, when such a temperature is reached that appreciable amounts of water are liberated due to decomposition, the gas-temperature curves become relatively steep and in course of time almost parallel to the volume axis.

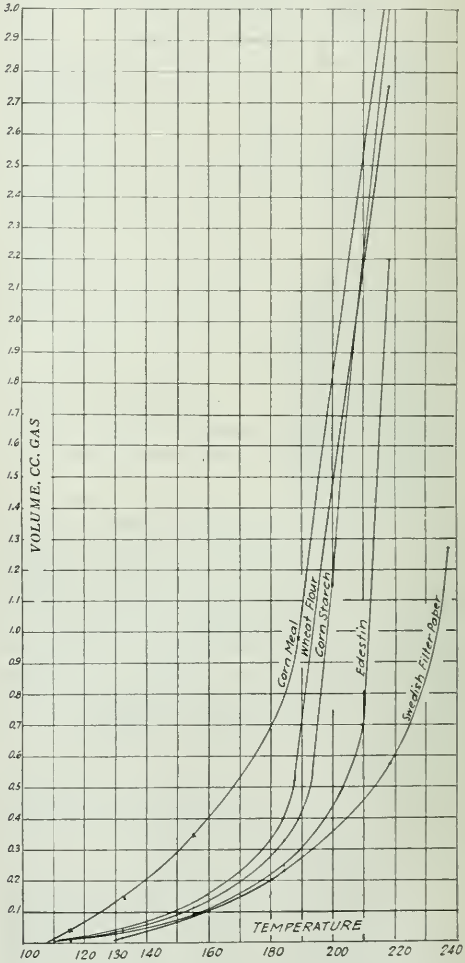

Fig 4

As will be seen from the tables, the periods for which we heated the samples ranged from 3 to 6 hrs. At the higher temperatures it is not necessary to continue heating much over 3 hrs., while at temperatures between 110° C. and 184° C. the heating should be kept up for about 5 hrs. We found in those runs in which we weighed the water liberated every hour or oftener that moisture continued to be given off for over 4 hrs. To give an example: It was found that on heating Swedish filter paper for 1 hr. at 184° C., 4.79 per cent water was obtained, while on continuing the heating for 4 hrs. more an additional 0.11 per cent moisture was liberated. Similar results were obtained in other cases.

SUMMARY

The method of determining the moisture contents of cereals and other colloidal organic substances outlined above consists essentially of heating the material in a very high vacuum for definite periods of time. The amount of moisture liberated is condensed quantitatively in a small tube surrounded by solid carbon dioxide from which it is accurately weighed.

Since the smallest amount of decomposition can be accurately determined, this method permits us to determine to what temperature and for what length of time a substance may be heated without encountering an appreciable amount of water from decomposition. Observations on the evolution of gases and moisture where measurable decomposition was taking place gave us an idea of the rate of decomposition at these temperatures.

LABORATORY EXPERIMENTS ON THE MANUFACTURE OF CHINESE ANG-KHAK IN THE UNITED STATES

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Received May 29, 1919

Chinese red rice, or ang-khak (ang-quac),[1] is produced by means of a noteworthy fungus, *Monascus purpureus* Went. Red rice evidently originated in one of the provinces of China, and even to-day may be procured only in certain localities of that country. It is well adapted to its special use, the coloring of food products, such as Chinese cheese, because of its property of breaking into fine particles when rubbed or brought into contact with watery solutions. The Chinese have been very secretive concerning the preparation of red rice, and the literature contains only the following facts on the subject. Ordinary rice is moistened and somehow infected or inoculated with a fungus which under humid conditions produces cottony mycelium, eventually binding the rice grains together. The rice grains, at the end of a brief period, are thoroughly impregnated with mold hyphae which produce the red color. When ready for the market, the red rice, the grains of which may be readily powdered between the fingers, imparts a clear carmine color to any moist food substances to which it is added. This same fungus is, according to Went,[2] responsible for the red rice of the Malay Islands, and is also employed in Formosa in making anchu, a rice drink.

Monascus purpureus has been reported from silage in America by Buchanan.[3] We have also obtained it repeatedly from silage where it grew in a substratum 6 in. below the surface, and also from spoiling cornmeal samples. Notwithstanding the competing organisms, *Monascus purpureus* has always been successfully isolated from Chinese red cheeses, which are colored with red rice. A culture of the same or a closely related mold has also been obtained from moldy carob beans. The most interesting source of all, however, is "freckled" codfish. We have not completed experiments to prove that the "freckling" is due to *Monascus purpureus*, but we have observed curious spore-like bodies, which in part compose the freckles, develop into the fungus in question when transferred to highly salted agar plates. The medium used was Czapek solution agar, slightly acidulated with normal lactic acid, and modified by the addition of 15 per cent sodium chloride. The spore-like bodies, transferred from the codfish "freckles,"[1] remained apparently unchanged on the agar surface of the plate for weeks, during which time the medium evaporated and the salt appeared as crystals in the agar and on its surface. Careful microscopic examination of these plates showed that the spore-like bodies developed in this concentrated material. The mold growth continued microscopic in area long enough for the plates to be overlooked. On reëxamination this microscopic growth had developed into a local, living, white fluffiness of mold hyphae, bearing the monilia-like spores of *Monascus purpureus*, and showing under the microscope the characteristic ascus-like bodies.

The chief interest of this investigation is the production of the red color. Lafar claims for red rice a clear carmine to gray-red color on pulverization. Buchanan's *Monascus purpureus* from silage grew on silage agar and broth, and on gelatin solutions, with the production of white to red to deep carmine mold growth, according to the age and the food given. On rice flour medium the surface mold growth was gray, with the medium a brilliant carmine.

Two strains of *Monascus purpureus* from silage, sent in by A. R. Lamb, of Iowa State College, were retained and studied[2] in the Microbiological Laboratory. One, A, is a more or less floccose fungus of a white, soiled white, or gray color; the other, B, is similar to Buchanan's organism in its color reactions, and it grows in a submerged manner. Four strains of *Monascus purpureus* were secured from Chinese products, three from the superficial red coloring on soy bean cheeses and one from red rice. Each shows some variation from the others in the intensity of the color reaction and rate of growth under the same conditions. Nevertheless all are apparently morphologically alike, and duplicate the description of Buchanan, Went, Ikene,[3] Uyeda,[4] and Harz.[5]

The laboratory experiments with the pure culture manufacture of red rice were begun in December 1917.

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[1] F. Lafar, "Handbuch der technischen Mykologie," **2**, 265–269, Jena, 1906.

[2] *Ann. Sci. Nat. Bot.*, **1** (1895), 1–16, plates 1 and 2.

[3] "*Monascus purpureus* in Silage," *Mycologia*, **2** (1910), 99–106, plates 22 and 23.

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[1] A. W. Bitting, "Preparation of the Cod and Other Salt Fish for the Market," U. S. Dept. of Agr., Bureau of Chem., *Bulletin* **133** (1911), 1–63.

[2] Czapek solution agar with 3 per cent sucrose was used as a standard medium.

[3] "Über die Sporenbilding und Systematische Stellung von *Monascus purpureus* Went," *Ber. botan. Ges.*, **21** (1903), 259.

[4] *The Botanical Magazine, Tokyo*, **15** (1902), 160.

[5] "Physomyces heterosporus," *Botan. Centr.*, **41** (1890), 378, 405.

Water was added to unpolished, uncooked rice, and small amounts of this material were sterilized in Erlenmeyer flasks. Strain A from silage, strain C from red rice, and strains D and E isolated from cheeses, were used.

The silage organism gave a pink color to rice grains, and caused some of the grains to split into small portions, while others could be crumbled into smaller, hard particles. Strains C and D produced very deep, almost red-black color throughout the rice, but they broke down the grains so completely that the mass became slushy. In the belief that the softening might proceed still further with no definite results, the reddened rice grains were spread out on a paper and dried. On drying they became a brilliant to black-red, crumpled and shrunken, with grains adhering in small masses, and tough in texture. The mold discoloration penetrated almost completely. The use of strain E, also from Chinese soy cheese, resulted in more promising material. After being dried out from a somewhat slushy consistency, each grain of rice stood intact, although not plump or regularly defined. The superficial deep red layers crumbled in what was considered the approved fashion, but below these the rice was hard and pinkish as in the case of strain A. The material, however, was considered worthy of exhibition.

These laboratory products were compared with a sample of red rice collected in China by Dr. Yamei Kin, of the Bureau of Chemistry. In this typical sample each rice grain is a regular, clear-cut particle, of a deep but dull carmine color. On rubbing between the fingers, these red rice grains crumble into a tissue-like envelop formed by the exterior surface of the grain, and a very fine, soft red powder, the particles of which go into suspension in water and into solution in ethyl alcohol or chloroform as well as in other solvents.

A second experiment was laid out with exactness, replacing the rough, preliminary methods. Uncoated and unpolished rice was sterilized in Erlenmeyer flasks. After cooling, 25 per cent additional sterile water was added to some samples and 30 per cent additional sterile water to others.

The results obtained with strains A, C, and D are worthy of note. On rice to which 25 per cent of water was added, strain A grew with a most delicate rosy color, and caused a somewhat more complete disintegration of the rice grains than in the preliminary experiment. It did not grow at all on the rice to which 30 per cent of water was added. It is evident, then, that less than 25 per cent of water should be added to obtain red rice. Strain C produced a dull, orange-red color on rice to which the 25 per cent of water had been added. The grains adhered occasionally, and when an attempt was made to crush them they merely split into smaller hard portions. The same results were obtained when 30 per cent additional water was used, except that a rather noticeable amount of close, felty mycelium, cementing the grains together, was obtained. It is believed that too much water is an inhibiting factor here. On rice to which 25 per cent of water was added, strain D actually produced reddened rice kernels, which may without hesitation be called American-made Chinese ang-khak. The rice kernels, which were well shaped, each intact in itself, and of a rich carmine-red, crumbled to powder between the fingers, and the outer layers resembled a tissue-like coating. Thirty per cent additional water caused this strain to act like strain C, the material, however, being tougher, more floccose, and entirely unsatisfactory.

Evidently rice which contains an addition of 25 per cent of water, when held at room temperature (22–24° C.), is at a critical point, so far as the various strains of *Monascus purpureus* Went are concerned. This fungus, although employed commercially only in the Orient, is more cosmopolitan in its habits than its applied use would indicate. Apparently, *Monascus purpureus* Went is a specific name applicable to a group of strains having a rather consistent morphology, but varying greatly in their quantitative production of the same substances.

SUMMARY

I—The characteristics of red rice, a common Chinese vegetable color used in food products, are due to a mold.

II—This mold, known as *Monascus purpureus* Went, although apparently found outside the Orient, is utilized in this way only in China.

III—All strains of *Monascus purpureus* are not adapted to the production of red rice, since each varies quantitatively in its physiological activity. Only those strains which produce a rich dark red growth throughout rice with a water content low enough to permit well-appearing grains in the finished product are acceptable for this purpose.

THE EFFECT OF MOLD UPON THE OIL IN CORN

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Received July 23, 1919

Under certain conditions of storage, corn undergoes spoilage induced largely by an excess of moisture and usually manifested by a moldy appearance. A common mold which attacks corn under these conditions is *Penicillium*, the growth of which necessarily causes deterioration, the extent and nature of which depends upon the length of the growing period of the mold and the particular constituents of the corn which are subject to decomposition. From the general appearance of corn attacked by this mold it is evident that changes are taking place in the grain and it was for the purpose of studying the effect of the mold upon the fatty oil in the corn that this investigation was undertaken. It is natural to assume that as the time period during which the mold is allowed to grow, increases, certain constituents of the corn are contributing to the growth and are therefore undergoing change, while certain other compounds are possibly being metabolized by the mold. The fatty oil belonging to

TABLE I—DESCRIPTION, TIME OF SPOILING, PERCENTAGE OF MOISTURE AND OF OIL IN CORN SAMPLES, AND PHYSICAL PROPERTIES OF THE OILS

SAMPLE	CONDITION	Time of Spoiling Days	Moisture Per cent	Oil (Calculated on Dry Weight) Per cent	PHYSICAL PROPERTIES OF THE FIXED OIL				
					Color	Odor	Taste	Specific Gravity	Refraction
1	Market sample, fair condition. Kernels yellow in color	..	21.9	5.58	Pale brownish red	Mild, fatty	Bland, fatty, becoming slightly bitter	0.9204 (23° C.)	1.4712 (23° C.
2	Most of corn affected with mold. Kernels gray and dirty. Musty odor	17	18.2	4.33	Pale brownish red. Some solid matter separated on standing	Strong, fatty, slightly acid	Fatty, becoming bitter	0.9228 (23° C.)	1.4722 (23° C.)
3	Whole mass of corn affected with mold. Dirty gray in color. Intense moldy odor	34	20.1	2.67	Brownish red. Darker than Nos. 1 and 2. Considerable yellowish solid matter separated on standing	Strong, musty. Disagreeable, sour	Fatty, strongly bitter	0.9212 (23° C.)	1.4725 (23° C.)
4	Dirty gray mass with strong musty odor. Yellow color of kernels gone	55	21.62	2.06	Very dark brown. Much solid separated on standing	Disagreeable, strong, sour, musty	Strongly bitter	0.9307 (24° C.)	1.4780 (24° C.)
5	Dirty gray, moldy, solid mass, with strong, offensive odor	90	17.0	2.02	Dark, reddish brown, almost black. Large portion of oil became semi-solid	Intensely strong, disagreeable, sour, musty	Strongly bitter, moldy	0.9444 (24° C.)	1.4800 (24° C.)

the former class of substances forms the basis of this paper, in which are discussed the general changes which take place in its content and composition.

Under favorable conditions the fatty oil contained in the germ of the corn readily becomes rancid, as do other oils under the same conditions. The development of rancidity is accompanied by more or less severe changes in the composition of the oil, which is evidenced by a noticeable difference in its taste and odor due to the formation of certain compounds of acid, aldehydic, or ketonic character. The prime object of this work was to study what changes, if any, take place in corn oil due to the growth of *Penicillium* on the corn.

A small part of a market sample of corn, presumably in the condition in which it is ground into meal, was taken for oil determination, and the remainder was placed in a large stone jar and inoculated with the mold *Penicillium* and set aside. After a short period a second sample of the corn was taken for analysis and the remainder again set aside. This sampling was continued at intervals for a period of 90 days, four samples of the spoiled corn being obtained in all.

Determinations were then made of the moisture and oil content of each sample. Physical constants and chemical examination of the mixed acids (insoluble acids), liquid and solid acids of each oil were also determined in order to enable comparisons to be made. All determinations were made according to the methods prescribed by the Association of Official Agricultural Chemists.[1]

For the purpose of comparison the several samples taken were described as to condition, general appearance, and time of spoiling. The percentage of moisture and of oil in the corn samples, and the physical properties of the oils, including color, odor, taste, specific gravity and refraction, were added to the data and are given in Table I.

It will be observed from Table I that as the mold progressed in growth the original yellow color of the corn kernels was gradually displaced by a dirty gray until the whole developed into a solid mass, while the musty or moldy odor gradually became more offensive.

The percentage of moisture fluctuated slightly during the first 55 days, dropping to the lowest point at the end of 90 days, when the mass of corn kernels was hardly recognizable.

A constant decrease was noted in the oil content of the samples, from 5.58 per cent in the market sample to 2.02 per cent in the thoroughly decomposed sample. Likewise the color of the oil became progressively darker with an increased amount of solid matter separating. The odor of the oil from Sample 1, which was mild and fatty, developed into a very strong, musty, and disagreeable odor, while the taste gradually became very bitter and moldy.

The first indication of any noteworthy change in the composition of the oils is displayed in the specific gravities and indices of refraction, both of these physical constants increasing in magnitude as spoiling developed.

CHEMICAL EXAMINATION OF CORN OIL SAMPLES

In order to show the changes in the oils as observed from the examination of the physical properties, a careful analysis of each sample was made with respect to acid, saponification and iodine values, and the percentage of volatile acids (Reichert-Meissl value), soluble acids, insoluble acids, acetyl value and unsaponifiable matter (Table II).

TABLE II—CHEMICAL PROPERTIES OF OILS FROM CORN SAMPLES

OIL SAMPLE	Acid Value	Saponification Value	Iodine Value	Volatile Acids (Reichert-Meissl)	Soluble Acids (Calculated as Butyric) Per cent	Insoluble Acids (Hebner Number) Per cent	Acetyl Value	Unsaponifiable Per cent
1	13.6	190.3	121.0	12.8	1.3	93.6	15.3	4.13
2	46.7	191.7	121.3	2.95	1.5	90.5	10.6	9.9
3	84.6	192.4	120.4	2.23	3.28	92.3	61.1	10.8
4	68.7	185.1	119.9	2.92	2.35	91.7	28.4	15.3
5	72.1	126.6	96.6	Insufficient oil	4.05	....	68.4	25.4

The acidity of the oil samples shows a general increase of considerable magnitude. Sample 1 exhibits a rather high acid value which is probably accounted for by the fact that the market sample was only fair in condition and contained a high percentage of moisture, which was more or less conducive to spoilage. After the first sampling the acid value of the oil had increased more than threefold. The highest acid value was found in Sample 3 at the end of 34 days of spoilage, followed by slight diminution in Samples 4 and 5 at the end of 55 days and 90 days, respectively.

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[1] H. W. Wiley, "Official and Provisional Methods of Analysis," J. Assoc. Official Agr. Chemists, U. S. Dept. of Agr., Bureau of Chemistry, *Bulletin* 107 (Rev.).

TABLE III—PHYSICAL AND CHEMICAL PROPERTIES OF MIXED ACIDS (INSOLUBLE ACIDS) OF OILS FROM CORN SAMPLES

Oil Sample	Color	Odor	Taste	Specific Gravity	Refraction	Neutralization Value	Iodine Value
1	Light yellowish brown	Fatty	Bland, fatty	0.9038 (22° C.)	1.4659 (22° C.)	184.8	129.1
2	Brownish red	Fatty, not agreeable	Fatty, bland, becoming bitter	0.9055 (23° C.)	1.4653 (23° C.)	183.2	142.2
3	Reddish brown	Fatty, disagreeable, musty	Fatty, becoming bitter and unpleasant	0.9071 (24° C.)	1.4672 (24° C.)	188.8	126.6
4	Brown	Disagreeable, fatty, rancid	Very bitter, fatty	0.9169 (23° C.)	1.4700 (23° C.)	186.5	122.9
5	Dark brown	Rancid (semi-solid)	Disagreeable, bitter	....	....	114.8	...

TABLE IV—PHYSICAL AND CHEMICAL PROPERTIES OF LIQUID ACIDS OF OILS

Oil Sample	Yield Per cent	Color	Odor	Taste	Specific Gravity	Refraction	Neutralization Value	Iodine Value
1	84.4	Light reddish brown	Mild, fatty	Fatty, slightly acid, becoming bitter	0.9105 (22° C.)	1.4674 (22° C.)	184.4	146.5
2	80.0	Brownish red	Fatty, bland	Fatty, becoming bitter	0.9087 (23° C.)	1.4670 (23° C.)	185.8	153.0
3	79.5	Dark brown	Faint, fatty	Fatty, bitter	0.9110 (24° C.)	1.4665 (24° C.)	175.3	135.3
4	82.7	Dark brown	Unpleasant, fatty	Fatty, becoming bitter	0.9194 (23° C.)	1.4730 (23° C.)	171.7	132.8
5	....	Insufficient oil for separation of liquid acids						

TABLE V—PHYSICAL AND CHEMICAL PROPERTIES OF SOLID ACIDS OF OILS

Oil Sample	Yield Per cent	Appearance	Odor	Taste	Melting Point Deg. C.	Neutralization Value
1	11.1	Pale yellow, tallow-like	None	Tallow-like	55–58	207.9
2	10.3	Pale yellow, waxy	None	Tallow-like	55–56	208.4
3	12.6	Pale yellow, waxy	None	Tallow-like	52–55	214.2
4	9.09	Darker yellow	None	Tallow-like	53–56	...
5	....	Insufficient oil to make separation of solid acids				

In saponification values the same general increase is noted in Samples 1, 2, and 3, followed by a decrease in Sample 4 and a sharp decline in Sample 5, indicating a consumption or decomposition of the glycerides at this point.

The iodine values remain almost constant in the first three samples, with a decided decrease in Samples 4 and 5, indicating a lowering of the content of unsaturated acids.

The high percentage of volatile acids in the original oil and the extremely sharp decrease, remaining almost constant, in the remaining oils points to the possible decomposition of these constituents by the mold as rapidly as formed.

The formation of soluble acids apparently was assisted by the gradual spoilage of the corn. The formation of insoluble acids, on the other hand, appears to have been retarded slightly after the molding began.

The acetyl value, which is a measure of the hydroxylated glycerides, exhibits noteworthy fluctuations, being especially high in Samples 3, 4, and 5, showing a rapid formation of these constituents as the experiment progressed.

One of the most remarkable changes brought about by the growth of the mold was the formation of unsaponifiable substances in the oils, a steady increase to 25.4 per cent having been found. It is very probable that the solid matter mentioned in the discussion of Table I, and which was observed increasing in each sample of oil, consisted largely of unsaponifiable substances elaborated from the oil by the mold.

INSOLUBLE ACIDS OF OILS FROM CORN SAMPLES

The insoluble acids (mixed acids) obtained from each sample of oil were subjected to physical and chemical examination (Table III.)

LIQUID AND SOLID ACIDS OF OILS

A separation of the liquid and solid acids was made from the insoluble acids by methods prescribed by the Association of Official Agricultural Chemists.

The physical and chemical properties of the liquid acids were determined (Tables IV and V).

The yields of liquid acids are shown to fluctuate considerably, a lower yield being indicated in oil from the moldy corn. The color, odor, and taste are also more pronounced in the moldy samples. A slight increase is observed in the specific gravity and refraction of the most moldy samples. The neutralization values and also the iodine values of these same samples are noticeably lower than the acids from less spoiled samples, indicating a decomposition of these acids during spoilage.

The yields of solid acids from the respective oils likewise differ, a perceptible drop being observed in Sample 4. The melting points also fluctuate. Neutralization values show slight increase as the spoilage continued, showing that a material effect was being produced even on the solid acids of the oils.

CONCLUSIONS

It may be stated that the effect of the spoilage of corn from the growth of mold was noticeably manifested in connection with the fatty oil. A consumption of oil by the mold was apparent, as manifested by the decrease in the yield of oil at each stage of decomposition. As regards composition of the oil, spoilage of the corn caused very decided increase in the free acids, the soluble acids, hydroxylated acids (acetyl value), and unsaponifiable constituents, with a decrease in the percentage of volatile acids, insoluble acids and unsaturated acids.

INSOLUBLE SOLIDS IN JAMS, PRESERVES, AND MARMALADES

By C. A. Clemens

SOUTH DAKOTA FOOD AND DRUG DEPARTMENT, VERMILION, S. D.

Received August 9, 1919

The official method for the determination of insoluble solids in fruit products[1] is slow and cumbersome. A method has been worked out which is rapid, easily manipulated, and at the same time obviously offers greater accuracy. By the substitution of an alundum crucible for a linen filter it becomes possible to apply suction and at the same time to have a better filtering medium, also to avoid one transfer of the insoluble residue. The only questionable point in the new procedure was the boiling of the sample instead of macerating with warm water, and this was shown by comparison of results with the official method to be permissible. This part of the procedure also avoids unnecessary transference of the residue.

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[1] *J. Assoc. Official Agr. Chemists*, [2] **2**, 177.

PROCEDURE

Twenty to twenty-five grams of the thoroughly macerated sample are weighed out into a 250-cc. beaker, 100 cc. distilled water added, the mass stirred, and the beaker covered with a watch glass. The solution is brought to a boil and allowed to boil for 5 min., when it is removed and transferred to an alundum crucible to which suction is applied. The residue is thoroughly washed with boiling water followed by 10 cc. alcohol and ether, respectively, dried in a water oven, cooled, and weighed.

Table I shows results obtained by this and the official method.

TABLE I

NATURE OF SAMPLE	A. O. A. C. METHOD	PROPOSED METHOD
Apple-blackberry preserves	0.57	0.58
Apple-blueberry preserves	0.28	0.27
Apple-gooseberry preserves	0.27	0.28
Apple-loganberry preserves	0.14	0.18
Apple peach preserves	0.31	0.26
Apple-raspberry preserves	1.20	1.25
Apple-raspberry preserves	0.88	0.88
Apple-raspberry preserves	0.48	0.50
Apple-raspberry preserves	0.64	0.60
Apple-raspberry preserves	0.70	0.70
Apple strawberry preserves	0.29	0.29
Apple-strawberry preserves	0.64	0.64
Apple-strawberry preserves	0.31	0.32
Apple-strawberry preserves	0.93	0.94
Apple-strawberry preserves	0.20	0.20
Apple butter	2.36	2.17
Glucose raspberry apple jam	1.10	1.09
Orange marmalade	1.05	1.00
Orange marmalade	3.50	3.55
Raspberry preserves	1.72	1.70
Raspberry preserves	3.85	3.87
Strawberry preserves	0.89	0.89
Strawberry preserves	1.85	1.81

A CHEMICAL STUDY OF THE ETHER EXTRACTS OF SOY BEAN LEAVES[1]

By E. M. Nelson

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Received July 5, 1919

The scarcity and high price of linseed oil during the last few years have led to extensive investigations directed toward obtaining a substitute which can be used in paint manufacture. Linseed oil has a high iodine number and forms a hard film upon drying; as yet no other oil has been obtained in large quantities which possesses these desired qualities. Soy beans give promise of becoming an important crop in this country because of the ease with which they can be grown and their high food value, and since they contain from 15 to 20 per cent of oil having an iodine number roughly from 115 to 145, attention is being given to the possibility of improving the quality of the oil by breeding. While engaged in making analyses of beans from pure lines and crosses grown by the Department of Genetics of the local Agricultural Experiment Station, the high iodine number of the ether extract of soy bean leaves suggested a possible source of a highly unsaturated oil. Ether extract waxes as well as oils, but if these latter compounds were made up of highly unsaturated fatty acids that fact might be of sufficient importance to warrant the perfecting of a method of separating them from other substances. A study of this problem shows that the highly unsaturated compounds obtained in an ether extract are not oils, but probably belong to the alcohol group of the waxes.

Upon saponification of a mixture of waxes and oils as obtained from an ether extract of soy bean leaves with a base such as caustic potash, soaps which are insoluble in ether are formed from the fatty acids of the oils and waxes. Chlorophyll also forms an ether-insoluble compound. The higher alcohols are set free and together with carotin can be extracted with ether. This affords a method for the partial separation of the fatty acids from the other material.

The following procedure was carried out to determine the possible relation of the fatty acids to the high unsaturation of the ether extract of soy bean leaves.

Leaves were collected from separate plants which were quite mature and dried at about 18° C. with the aid of an electric fan. When thoroughly dried the leaves were ground in a mill in such amounts as were to be used immediately. Only freshly ground material was used to prevent oxidation from atmospheric oxygen. Four or 5 g. were then extracted for 16 hrs. with about 20 cc. of anhydrous ether in a Soxhlet extractor, and the extract received in a 100 cc. Erlenmeyer flask. The ether was evaporated and the material saponified by boiling gently for an hour over a water bath with 25 cc. of alcoholic potash with a reflux condenser attached. The alcohol was then evaporated and the residue dried over night in a vacuum desiccator. In the morning about 50 cc. of water were added and the contents of the flask transferred to a separatory funnel, washing several times with water and ether. The aqueous solution with the insoluble material was then extracted with several 50 cc. portions of ether until there was no trace of color in the extract. The ether was distilled from the unsaponifiable material, the residue dried over night in a vacuum desiccator, and the iodine number determined according to the method of Hübl as described in Sherman's "Organic Analysis" (Revised). Ten cc. of 20 per cent sulfuric acid were added to the saponifiable material and extraction with ether and the iodine number determination completed as with the unsaponifiable matter.

Methods for this kind of work are not standardized as the nature of the material from different plants varies to such an extent that different courses of procedure have to be carried out. It was found that by using from 4 to 5 g. of dried leaves about 0.2 g. of extract was obtained and that this was the most convenient amount to handle without loss and on which to determine the iodine number. Some difficulty was experienced in extracting the unsaponifiable matter with ether because of the tendency to form an emulsion. This was largely avoided by using only a small amount of material and more water and ether, and a complete separation was usually obtained within 2 hrs. The extraction of larger amounts of material with the idea of running more than one iodine number from one separation did not prove feasible because of the tendency of the material to adhere to glass. About 1.5 g. each of the saponifiable and unsaponifiable material were dissolved in chloroform and the volume made up to 50 cc.; 10 cc. aliquots were then used to determine the iodine number. The checks obtained were no closer than from individual separations and the results were much lower.

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[1] Published with the approval of the Director of the Wisconsin Agricultural Experiment Station.

A number of determinations of the per cent of ether extract and the iodine number of this material were made to show the range of variation in different plants.

The results obtained are shown in Table I.

TABLE I

Plant No.	Ether Extract Per cent	Hübl Numbers Before Separation	Hübl Numbers —After Separation— Unsaponifiable	Saponifiable
1	5.59	110.4	.....	.....
2	4.04	120.9	.....	.....
3	3.92	123.8	.....	.....
4	4.20	125.7	.....	.....
5	4.72	109.7	148.4	104.2
			124.7[1]	98.9[1]
			122.3[1]	95.3[1]
			126.7[1]	101.1[1]
6	4.56	116.4	142.2	108.1
7	6.08	119.0	.....	.....
8	3.71	106.2	142.7	103.4
9	3.84	126.2	157.9	122.3
			158.2[2]	122.0[2]
10	4.24	114.4	.....	.....
11	5.11	118.3	149.9	113.6
12	5.16	116.6	.....	.....

[1] These results are from using aliquots of a chloroform solution of the saponifiable and unsaponifiable matter from Plant 5 as mentioned above.

[2] Duplicate of Plant 9.

From Table I it can be seen that the per cent of ether extract varies from about 3.7 per cent to 6.0 per cent in the air-dried leaf, and the Hübl number of the crude ether extract from 105 to 125. The Hübl number of the unsaponifiable material averages 149.7 and of the saponifiable 112.3, showing conclusively that the former has the higher degree of unsaturation. The compounds which are obtained in the unsaponifiable material are probably largely cyclic alcohols (such as phytosterol and stigmasterol) and carotin, and perhaps some other highly unsaturated alcohols.

Chlorophyll is not separated entirely from the fatty acids in the method used because upon boiling with alcoholic potash it forms the tribasic salt, potassium chlorophyllide. The phytol group is split off and recovered in the unsaponifiable extract. Carotin is a neutral compound which does not react with bases.

SUMMARY

The amount of ether-soluble extract from dry soy bean leaves is so small (3 to 6 per cent) that it is doubtful whether they would be a profitable source of paint oil, even if it were of good quality. The results obtained, however, show clearly that the most highly unsaturated compounds in the leaves of the soy bean are not oils but probably belong to the alcohol group of the waxes, which do not form a hard film on drying. For these reasons soy bean leaves do not form an available source of oil for paint manufacture.

PURIFIED CRESOL (CRESYLIC ACID)

By Herbert C. Hamilton

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Received July 12, 1919

One of the minor problems arising from the war because of interference with importations from Europe was that of obtaining a substitute or equivalent for trikresol, a proprietary article imported from Germany and extensively used as a preservative and disinfectant. As has been shown to be true in many other instances, it is equally true in this case that there is no lack in America either of crude material or of ability to purify it. There was required only the incentive.

Trikresol is so named because it is a mixture of the three isomeric cresols naturally occurring in coal tar. These three cresols are identical in composition, but have different physical and bactericidal properties. These differences, however, are unimportant and nothing of practical value results from their separation.

Trikresol, while useful as a general antiseptic and germicide, with a phenol coefficient of $2^{1}/_{2}$ to 3, found its most extensive application as a preservative for serums, vaccines, and similar biologic substances. Careful research has proved that for this purpose, with one exception,[1] no other antiseptic has been found entirely suitable, either because of its efficiency or the toxic or irritating action when absorbed from a hypodermic injection.

The cresols have practically the same toxicity as pure phenol, as shown in the accompanying table, but the corrosive action is so low and the germicidal value so high in comparison, that the use of phenol as a germicide is no longer logical. To illustrate: cresol with a coefficient of 3, when diluted 1 to 60, is equal in every respect to a 5 per cent solution of phenol, while the toxicity of the solution is only one-third as great because of the degree of dilution, and the corrosive action, while not measurable with accuracy, is less than one-third as great.

Superficially trikresol is identical with the cresols of coal tar, since an average sample of the latter contains not over 5 per cent of constituents other than the cresols. But it was very promptly observed that cresol, as it appears on the market under various names, is inapplicable for use as a serum preservative because of three specific reasons, all of which are interrelated, namely:

1—Incomplete solubility
2—Disagreeable odor
3—Color

Incomplete solubility is due to the presence of one or more of three substances, naphthalene, colored compounds formed apparently at the expense of the cresols, and phenols of higher boiling point and less solubility than the cresols.

The disagreeable odor is largely due to pyridine and partly to the naphthalene which have been incompletely separated in preparing the crude phenol.

The origin of the color which appears in cresol and phenol is more or less uncertain. It is probably not always due to the same cause, but may in some cases be due to impurities in the cresol, and in others, to incidental conditions, such as the effect of light or air or the action of alkali from the glass container.

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[1] Carl Voegtlin, Hygienic Laboratory, *Bulletin* 96.

It is said that the germicidal value of a highly colored lot is greater than that of a clear straw-colored sample. This, however, is probably a hastily drawn conclusion from insufficient evidence, since different lots are found to differ much more than a water-white and a colored sample from the same lot. Redistillation corrects the color and can improve the solubility and odor, but not to a sufficient extent.

The development of color appears to be a property not only of cresols but also of pure phenol and no method has been devised by which such a change can be entirely prevented. The coloring matter appears to be a new constituent and to have properties entirely different from those of the original cresols. It remains behind on redistillation, but further quantities form so that only the freshly distilled material is entirely colorless.

Gibbs[1] ascribes the development of color by the action of sunlight to a labile hydrogen atom and describes experiments with the three cresols in which coloration occurred in varying times with the different ones but all were affected in the same way.

This, however, does not explain the immediate cause of this coloration. A sample of a freshly redistilled lot was set in the sunlight and another was kept in an amber bottle in the dark. The first, after three months, was very slightly tinged with pink, the other was decidedly reddened. This is not an isolated case but was a careful demonstration of what frequently occurs in practice with large lots. Sufficient observations have not been made to arrive at a theory as to the cause or causes of the change and no method has consistently prevented its recurrence.

The disagreeable odor is due to pyridine and naphthalene which one would naturally think were eliminated in the process of separating the cresols from the creosote oil. In this process the acid constituents of the oil are combined with an alkali such as caustic soda or lime, and in this form should be readily separated from the neutral and basic substances. In fact only a very small percentage of these bodies remain with the cresols and are dissolved with it when its alkaline combination is broken up, as it is in practice, with carbonic or sulfuric acid. The odor of crude carbolic acid is not distinctly like either impurity, since the natural odor of the cresols masks the others until they are unrecognizable. Distillation carries these impurities over and little improvement can be accomplished by this step as the sole purifying process.

Nevin and Mann[2] depended on separation by redistillation to obtain the proper fraction but this, as noted above, while removing the colored and some of the insoluble impurities, fails to remove pyridine and naphthalene, which are responsible for the odor. While this odor is perhaps negligible, it is easy to detect the difference between two lots of cresol, one purified to remove the odorous impurities, as will be described later, and the other purified by redistillation only.

In my experiments an attempt was made to study the sodium cresylate compound when prepared in molecular proportions. In concentrated solution no observable separation takes place to indicate that purification by this means is feasible but on further dilution the naphthalene crystallizes out in a well-recognized form and often in considerable quantities. This can be filtered out, but on again recovering the cresols no material improvement in odor results, because the naphthalene is the less objectionable of the two.

My next experiments were carried out having in mind the examination of sodium cresylate in solid form to see if impurities could be detected, identified, and removed by tests applied to the dried or crystallized material.

In the process of evaporating the solution it was observed that the vapors smelled distinctly of pyridine, and further, that after a certain time no odor of this character could be detected. Carrying this experiment to its conclusion and recovering the cresols, they were found to be practically free from the objectionable odor of the crude cresols and on redistillation a water-white soluble product was obtained with no odor but that of the pure cresols.

The practical working out of this process is as follows: Dissolve the crude cresol in a solution of caustic soda molecularly equivalent, using sufficient water to dilute the sodium cresylate to a 25 per cent solution. Then boil, or drive live steam through the solution until the odorous impurities have passed off with the steam. If the solution is boiled over an open flame, care is necessary to avoid concentrating the solution too much as the cresylate breaks up and free cresol is volatilized and may take fire. It is important to add water to replace that lost by evaporation.

The time necessary to vaporize the impurities varies with the amount present, and can be determined by smelling. "The nose knows" when the pyridine is gone. The solution should be allowed to become cold and then observed to see if naphthalene or other neutral oils are present. Any floating oil can be skimmed off, while the naphthalene, if any remains unvolatilized, can be removed by filtration or centrifuging.

Treatment with sulfuric acid equivalent to the alkali originally used will break up the cresylate and set free cresol which can be recovered as a supernatant layer over the sodium sulfate solution. Separation should be very complete, as the water otherwise present causes trouble in distilling.

The removal of these two impurities, which rarely amount to more than 5 per cent of the cresols, is therefore equivalent to a complete purification of the substance, since the color is automatically removed by redistillation, and a careful observation of the temperature of distillation at the end of this step insures the removal of the higher boiling phenols which are less soluble than the cresols and may for that reason be considered as impurities.

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[1] *J. Am. Chem. Soc.*, **34** (1912), 1190.

[2] *Ibid.*, **1917**, 2752.

TOXICITY ASSAY

Sample.......................Purified cresols
Animal.......................Guinea pigs
Method.......................Subcutaneously

WT OF ANIMAL	CRESOL DOSE PER KILO	RESULT
0.572	0.6	Recovered
0.611	0.6	Recovered
0.557	0.7	Died
0.640	0.7	Died
0.572	0.8	Died
	PHENOL	
0.437	0.5	Recovered
0.480	0.5	Recovered
0.446	0.6	Died
0.480	0.6	Died
0.570	0.6	Died
0.340	0.7	Died

Toxicity about 90 per cent of that of phenol: Worth Hale, Hyg. Lab., *Bulletin* **88**; James Leake and Hugh B. Corbin, Hygienic Laboratory, *Bulletin* **110**.

GERMICIDAL ASSAY

Sample...........Purified cresols
Method...........A. P. H. A. phenol coefficient method[1]
Organism.........*B. typhosus*

DILUTIONS SAMPLE	TIME AND RESULTS 5	10	15	20
1–300	—	—	—	—
1–350	—	—	—	—
1–400	+	—	—	—
1–450	+	+	—	—
1–500	+	+	+	+
PHENOL				
1–100	—	—	—	—
1–110	+	—	—	—
1–120	+	+	—	—
1–130	+	+	+	+
1–140	+	+	+	+

Coefficient 3.6

[1] Committee Report, *Am. J. Pub. Health*, **8** (1918), 506.

The cost of the process is inconsiderable, since no complicated chemical or mechanical steps are necessary. It is evident from observation of the steps in the process that no unusual equipment is needed and only the commonest chemicals are employed. It is evident, therefore, that here again the German chemists profited at our expense for many years while the crude materials waited only for proper development.

The logical place for the economical production of the refined cresols is where the crude material is first separated from the oils distilled from coal tar. These crude phenols, necessarily dissolved in alkali to separate them from the neutral oils, can, at that point, by suitable means, be freed completely from their impurities, and after fractional removal of the phenol proper, the cresols could then be recovered in pure form with one operation.

The production of purified cresols is, therefore, a logical opening for American enterprise, as well as American resources, for here, as in Europe, are immense supplies of coal tar on which to draw for crude materials.

A NEW HEXABROMIDE METHOD FOR LINSEED OIL[1]

By Lawrence L. Steele and Frederick M. Washburn
U. S. BUREAU OF STANDARDS, WASHINGTON, D. C.

Received September 17, 1919

I—INTRODUCTION

It has been recognized for many years that the hexabromide, insoluble in ether, which is derived by the addition of bromine to linseed oil or its fatty acid, is a characteristic compound, the quantitative determination of which should be of the greatest importance in the examination of this oil for adulteration. Several methods for the determination of the hexabromide yield of linseed oil and its fatty acid have been published. In every case, the author obtained concordant results, but when the method was used by other analysts, the results reported were unsatisfactory. In some cases different workers using the same linseed oil obtained hexabromide yields as widely divergent as 30 and 50 per cent.

The authors of this paper first made a study of the published hexabromide methods and from the experience gained have developed a new hexabromide method by which it is believed concordant results can be obtained.

A preliminary study of the hexabromide compounds prepared from linseed oil as compared with the fatty acid hexabromide led the authors, for two main reasons, to concentrate their attention on those methods which involve the preparation of the latter derivative. In the first place, the hexabromide made from the fatty acids of linseed oil is more stable, has a sharper melting point and a better crystalline structure than the corresponding hexabromide derived from the glyceride. In the second place, our present knowledge of linseed oil does not tell us whether or not the linolenic acid is present quantitatively as a simple triglyceride. It is obvious that if mixed glycerides are present in linseed oil the hexabromide derived from that oil might be a mixture, instead of one definite compound.

In this article, only those hexabromide methods in which bromine is added to the fatty acids of linseed oil will be considered.

II—DISCUSSION OF HEXABROMIDE METHODS

In 1909, a representative committee of linseed oil chemists[1] in this country made a study of linseed oil in order to prepare specifications for its purity. One of the tests which was studied was the hexabromide yield of linseed oil glyceride by Tolman's method.[2] The results which were obtained were unsatisfactory. In 1911 the committee tried for the first time a hexabromide test on the fatty acids of linseed oil, employing the method of Hehner and Mitchell as described by Lewkowitsch.[3]

In brief, the method was as follows:

> The fatty acids of linseed oil were dissolved in glacial acetic acid and the mixture cooled to 5° C. and bromine to excess slowly added. The mixture was allowed to stand for 3 hrs., filtered on a Gooch and washed successively with 5 cc. each of chilled glacial acetic acid, alcohol, and ether. The precipitate was dried in a steam oven and weighed.

The results obtained by the committee with this method were uniformly low, the hexabromide yield running from 28 to 32 per cent. In the light of the higher results obtained by the Eibner method, to be described later, it is evident that this method was defective in the addition of bromine. In other words, the linolenic acid was not quantitatively converted to hexabromide under the conditions followed, or else the hexabromide which was formed did not quantitatively separate from the solvent in which addition of bromine was made.

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[1] Published by permission of the Director of the Bureau of Standards.

[1] A. S. T. M. Committee Reports, **1909**.

[2] THIS JOURNAL, **1** (1909), 340.

[3] "Chemical Technology of Oils, Fats and Waxes," **1** (1904), 365.

In 1913 a new hexabromide method was formulated by the linseed oil committee[1] but the results obtained were far from satisfactory, different analysts reporting as widely divergent hexabromide yields as 35 and 51 per cent on the same linseed oil. In brief, this method was as follows:

> The linseed oil was saponified with excess alkali, the fatty acids were liberated, washed with water until neutral and filtered through dry paper. One gram of fatty acids was dissolved in 50 cc. of absolute ether, the mixture cooled to 4–6° C. and bromine added slowly to excess. The mixture was allowed to stand at 4–6° C. for 30 min. and then filtered on a Gooch, washing with four 20-cc. portions of cold absolute ether. Washing by decantation, using a centrifuge, was an optional method. The precipitate was dried in a water bath and weighed.

The results obtained by members of the committee indicate that in some cases a quantitative addition of bromine to linolenic acid was attained, while it is believed that the low results reported in other cases can be explained only by incomplete addition of bromine or by incomplete crystallization of hexabromide from the solvent used during the addition of bromine. One of the members of the committee reported excellent results by the use of the Eibner[2] hexabromide method, published the year before. This new method looked extremely promising and was given a thorough trial by the committee in 1915 and again in 1916. One member reported consistently good results by the new method, but other members working on the same linseed oil failed of agreement, and at last the committee came to the decision that Eibner's method possessed difficulties which at that time precluded its use as a part of a linseed oil specification.

Since the Eibner method seemed to be by far the best hexabromide method which has been published, the authors undertook to study it in detail. This method as published is exceedingly long and tedious, especially in the preparation of the fatty acids. For the sake of brevity, this method will be only outlined, but several points will be criticized and sources of error will be pointed out which it is believed account for the unsatisfactory results obtained.

The salient features of the Eibner method are:

> The linseed oil is saponified with excess alcoholic potash, the fatty acids are liberated with mineral acid and extracted with ether. The ether solution is dried over anhydrous sodium sulfate, the ether evaporated, and the fatty acids are dried in a water bath in a stream of dry hydrogen. The accurately weighed fatty acids are dissolved in a definite amount of ether (dried over calcium chloride). An aliquot portion of this solution is cooled to —10° C., or below, and exactly 1 cc. of bromine added very slowly, the low temperature being maintained. The mixture is then allowed to stand at a temperature between —10° C. and —5° C. for exactly 2 hrs., then filtered on a Gooch and washed with five 5-cc. portions of cold ether, suction being used after the last washing only. The precipitate is dried at 80° to 85° C., cooled, and weighed.

Lewkowitsch[3] criticizes Eibner's preparation of fatty acids in that the method is unnecessarily elaborate in detail. It is believed that if Eibner's directions are carefully followed, the fatty acids thus prepared are pure, but a very much shorter method will give equally good results.

Eibner dissolves the dried fatty acids in ether "dried over calcium chloride." The alcohol and water content of ether so prepared will be variable, depending upon a number of factors: length of time of drying, amount of calcium chloride used, and size of particles of the drying agent. As will be shown later, small amounts of alcohol in the solvent seem to influence to a marked degree the addition of bromine to the fatty acids of linseed oil when they are dissolved in chloroform. It seems quite possible that variable results might be obtained in his method because of variable quantities of alcohol or water in different lots of ether used as solvent for the fatty acids.

The procedure of preparing a 10 per cent solution of the fatty acids in ether is open to the objections that evaporation of ether will take place during the measuring of the aliquot portion and the volume of ether varies quite appreciably with the temperature. Errors in the amount of fatty acids taken for analysis would be liable to result from this procedure.

The use of ether as a solvent for the fatty acids during the addition of bromine is open to the objection that solid bromine derivatives separate from the solution before an excess of bromine has been added and it is conceivable that partially brominized derivatives might crystallize and thus resist further addition of bromine and thereby lead to low results.

After the addition of bromine to the fatty acids, the mixture is allowed to stand with excess of bromine for 2 hrs. before filtration in order to insure complete crystallization of the hexabromide. It is possible that under these conditions some substitution of hydrogen in the hexabromide by bromine might take place.

It is believed that the most probable cause of variable results is the method of filtration and washing of the hexabromide precipitate. A finely divided precipitate would filter very slowly on the Gooch and considerable amounts of ether would be lost by evaporation. It would be hard to wash such a precipitate free from impurities, while a more crystalline precipitate in another determination would filter faster and could be washed more efficiently. Eibner does not specify the quality of the wash ether. It is quite probable that U. S. P. ether would give different washing efficiency than ether dried over sodium, for example.

Eibner considered the hexabromide sufficiently washed when it was white and free from yellow material. It will be shown in the experimental part of this article that after a hexabromide precipitate has been washed free from yellow material, further washing with ether removes considerable amounts of white material which is not hexabromide. The fact that he dries the hexabromide at 80° to 85° C. and states that drying at 100° C. is apt to cause sintering is very good proof that the material is not pure hexabromide. As will be shown later, a properly washed hexabromide precipitate can be safely dried at 110° C., with no sign of sintering or other deterioration.

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[1] Proc. A. S. T. M., **1913**, p. 373.

[2] *Farben-Ztg.*, November 23, 1912 (No. 8).

[3] "Chemical Technology of Oils, Fats and Waxes," **1**, p. 573, 5th Ed.

After the published hexabromide methods had been studied, an outline of a new method was developed which was designed to eliminate the errors believed to be inherent in the Eibner method and the other methods described. It was proposed to dissolve the fatty acids of linseed oil, prepared by a suitable method, in such a solvent as carbon tetrachloride or chloroform, in which the hexabromide was known to be somewhat soluble, and to add an excess of bromine to the cooled mixture. The solvent was then to be removed by evaporation and the resulting mixture of hexabromide contaminated with other bromides washed until pure with a solvent like ether, in which the hexabromide was known to be only slightly soluble. It was believed that the procedure outlined above would eliminate errors due to irregular addition of bromine.

III—EXPERIMENTAL DEVELOPMENT OF NEW HEXABROMIDE METHOD

A. PREPARATION OF FATTY ACIDS—The method for the preparation of the fatty acids of drying oils given by Lewkowitsch[1] was tried and gave excellent results. This method is very simple and rapid, and the determination of the iodine number of the fatty acids indicated that they were not appreciably oxidized. For example, a linseed oil having an iodine number of 181 (Hanus) yielded by this method fatty acids having an iodine number of 185 (Hanus). This method was therefore adopted without further investigation. It was decided that it would be more accurate to weigh out the sample of fatty acids for each hexabromide determination, rather than to make up a standard solution of the fatty acids in the solvent to be used and then pipette aliquot portions.

B. ADDITION OF BROMINE TO FATTY ACIDS—(*1*) *Choice of Solvent.* Chloroform was selected because it was known that the hexabromide was moderately soluble in this solvent and because it is commonly used as a solvent in various reactions involving bromine and the other halogens. After some experimentation it was found that the hexabromide formed from one gram of fatty acids was sufficiently soluble in 10 cc. of chloroform at —5° C. to prevent its precipitation during the addition of bromine.

(*2*) *Effect of Added Impurities in Solvent.* The first chloroform used was of U. S. P. quality. Later some chloroform was carefully washed with water to remove alcohol and then dried with calcium chloride and redistilled. When this pure material was used as a solvent, the hexabromide yield suddenly dropped from an average value of 46 per cent to about 28 per cent.[2]

After some time, this drop in hexabromide yield was traced to the absence of alcohol in the chloroform. Different lots of chloroform were made up containing varying amounts of absolute ethyl alcohol. It was found that the presence of 0.50 per cent of alcohol in the solvent increased the hexabromide yield from 28 per cent for pure chloroform to 43 per cent. Mixtures with 3 and 5 per cent alcohol gave the maximum yield of 46 per cent. Amounts of alcohol as high as 10 per cent lowered the hexabromide yield to 43 per cent. In order to gain some insight into the action of alcohol in the solvent during addition of bromine to the fatty acids, various other materials were added to chloroform in small amounts and the mixtures were used as solvent in a hexabromide determination.

It was found that 3 per cent of benzene gave a hexabromide yield of 29.6 per cent or practically the same as pure chloroform. Three per cent of methyl alcohol gave a 43 per cent yield, while 3 per cent of acetone gave 42.8 per cent. In order to see whether traces of hydrobromic acid catalyzed the quantitative addition of bromine to the linseed fatty acids, some gaseous hydrobromic acid was passed into pure chloroform and the mixture used as solvent in a hexabromide determination. The yield obtained in this case was 36 per cent.

The authors are at the present time at a loss to explain why 3 per cent of ethyl alcohol in chloroform gives the maximum and constant yield of hexabromide.

(*3*) *Conditions for Addition of Bromine.* After a suitable solvent for the fatty acids during addition of bromine had been found, a study of other factors entering into the reaction was made. Determinations were made in direct sunlight, in ordinary diffused daylight, and in a dark room. No difference was noted between results obtained in the dark and in ordinary daylight, but results slightly variant were obtained when the addition of bromine was made in direct sunlight. It is therefore specified that direct sunlight should be avoided during addition of bromine. The length of time for the bromine-fatty acid mixture to stand after an excess of bromine has been added was found to be practically immaterial. The same results were obtained when the tube stood from 30 min. to 1 hr. as when the time of standing was 10 min. In all known methods the standing of the brominized solution was important in order to insure complete precipitation of hexabromide before filtration. Since in this new method the solvent is evaporated, there is no need of allowing the mixture to stand to induce crystallization of the hexabromide. It was decided to allow the mixture, after addition of bromine, to stand 10 min. in order that the reaction should be complete. In all cases this length of time was found to be sufficient. The optimum temperature for the addition of bromine was found to be about —5° C. because it was low enough to prevent local heating with subsequent substituting action by the bromine, and not so low as to cause the hexabromide precipitate to crystallize in a too finely divided condition, thereby increasing the difficulty of washing.

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[1] "Chemical Technology of Oils, Fats and Waxes," 1, p. 109, 5th Ed.

[2] All hexabromide yields given, unless otherwise stated, are on a single sample of raw linseed oil of known purity with an iodine number of 181 (Hanus).

C. ISOLATION OF THE HEXABROMIDE—(*1*) *Evaporation of the Solvent.* It was obvious that if a solvent such as chloroform, in which the hexabromide was soluble during the addition of bromine, was used, the hexabromide could not be quantitatively removed by filtration or decantation. In the first determinations the chloroform and excess bromine were evaporated by attaching the tube to a vacuum pump. This proved to be tedious because the evaporation cooled the solvent and greatly slowed up the process. Passing a stream of dry air through the tube aided the evaporation to some extent, but the following better method was finally devised. Amylene was added to absorb the excess of bromine. (This substance is an unsaturated hydrocarbon of low boiling point which readily reacts with bromine.) Heat could then be applied during the evaporation of the chloroform without the possibility of substituting action of bromine on the hexabromide at elevated temperatures. This variation in the procedure gave very satisfactory results. Only a few drops of the amylene were necessary and any excess would be evaporated with the chloroform. The dibromamylene formed was found to be readily soluble in ether, so that no difficulty resulted from contamination of the hexabromide by this halogen derivative.

Experience showed that it was necessary to remove the chloroform quantitatively from the impure hexabromide before the washing with ether; otherwise low results were obtained through solution of the hexabromide in the ether-chloroform mixture. It was found that all chloroform could be removed, if, after the chloroform solution of bromides was evaporated to a thick paste, the tube was immersed for two-thirds of its length in water at 60° C. for 15 min., while the tube was connected to a suction pump indicating a pressure not greater than 30 to 40 mm. of mercury.

(*2*) *Washing of the Hexabromide Precipitate.* The first washing of the impure hexabromide was done with cold absolute ether. It was decided at the start that washing would be more efficient by decantation, employing a centrifuge. In the first determinations made, the washing was continued until the precipitate was white and the wash ether colorless, the criterion of purity of precipitate employed in the Eibner method. Three 10-cc. portions of ice-cold ether were found to be sufficient to give white hexabromide in all cases. Since it was recognized that the hexabromide was somewhat soluble in ether, the washing was discontinued after the precipitate was white. A series of results was obtained by this method, the hexabromide yields varying from 48 to 51 per cent.

It was believed at that time that the varying results were due to different conditions in the addition of bromine. A series of determinations was made in which the conditions during the addition of bromine were varied in a large number of ways. An excess of bromine was added in direct sunlight, in diffused daylight, and in the dark, and the mixture in each case allowed to stand for lengths of time varying from 1 to 24 hrs. No conditions could be found under which concordant results could be obtained.

Finally a study was made of the washing of the hexabromide, and here was found the explanation of the irregularities in the results. By evaporating the various portions of wash ether, and weighing the residue, it was found that even after three washings, when the hexabromide precipitate was snow-white, further washing would still remove white solid material that was not hexabromide—enough other than hexabromide to lower the percentage yield from 50 or 51 per cent to about 46 per cent. This fact led to the decision that a more efficient washing of the hexabromide should be carried out.

It was determined that the hexabromide after washing with ether occupied a volume of about 2.5 cc. By experiment it was found that there were about 1.75 g. of oily bromides formed from 1 g. of linseed fatty acids. Using 20-cc. portions of wash ether, it was calculated that the first washing should remove approximately seven-eighths or 1.53 g. of the oily bromides. The second washing should remove seven-eighths of the amount remaining, or 0.19 g., and the third washing should remove seven-eighths of the amount remaining, or 0.028 g. The fourth washing should remove the small quantity of 0.0014 g., leaving the hexabromide practically pure.

In actual practice it was found that the theoretical efficiency of washing as given above was not reached. In an experiment it was determined that the following quantities of impurities were washed from the hexabromide formed from one gram of the fatty acids of linseed oil by four washings of 20 cc. of ice-cold absolute ether.

First washing	1.494 g.
Second washing	0.204 g.
Third washing	0.038 g.
Fourth washing	0.012 g.

The use of such comparatively large amounts of ether brought in the question of loss of hexabromide through solution in the ether. Lewkowitsch reports that the hexabromide of linolenic acid is very slightly soluble in cold ether, but gives no figures. A determination (see experimental part) showed the solubility of pure hexabromide in absolute ether to be 0.00026 g. per cc. at 0° C. and 0.00056 g. per cc. at 24.5° C. In order to obviate errors due to solution of hexabromide in the wash ether, it was decided to saturate the wash ether with hexabromide at 0° C. By this procedure loss of hexabromide through solution should be entirely eliminated.

In the preparation of the wash ether saturated with hexabromide, it was not found necessary to use pure hexabromide recrystallized from xylene. If the hexabromide from previous determinations were used, it would contain very small amounts of other bromides which would dissolve in the ether during saturation but would do no harm because there would be no tendency of these compounds to crystallize during washing of the hexabromide in the determination.

The use of ether in washing the hexabromide precipitate was inconvenient in one respect: it was necessary to keep the wash ether at some predetermined temperature during the whole process of washing, owing to the fact that the solubility of hexabromide in ether varies considerably with the temperature. An attempt was made to find some solvent in which the hexabromide was so slightly soluble that washing could be carried on at room temperature. Benzene (C. P., free from thiophene) was saturated with pure hexabromide at 28° C. and the solubility determined. Results indicated that benzene dissolved 0.000204 g. of hexabromide per cc. at this temperature. A hexabromide determination was made with benzene saturated with hexabromide at the room temperature as a washing medium. The results averaged 39.5 per cent, or about 6.5 per cent lower than those obtained with the regular wash ether. It is believed that this drop in hexabromide yield was due to the appreciable solubility at room temperature of hexabromide in a mixture of the oily bromides, contaminating the hexabromide, and the benzene.

Washing experiments were made in which ordinary 95 per cent alcohol and absolute alcohol were substituted for ether, but pure white precipitates were not obtained and these materials for washing were abandoned.

Washing experiments were made in which U. S. P. ether, instead of "ether over sodium," was saturated with hexabromide at 0° C. The results obtained were variable and slightly higher than those with the absolute ether and hence it was concluded that absolute ether should be specified in all cases as a washing medium.

(*3*) *Properties of Hexabromide.* (*a*) *Melting Points.* Lewkowitsch gives values for the melting point of the hexabromide of the fatty acid of linseed oil as 180° to 181° C. and 183° C. Various other values of this constant have been reported. The highest value is 183° C., while Eibner claims 177° C. to be the correct value.

The authors prepared some pure hexabromide by recrystallizing twice from hot xylene and washing with absolute ether until pure. When some of this material was heated slowly in a test tube to a temperature near its melting point evidence of decomposition was noticed and traces of hydrobromic acid were detected. On raising the temperature to the melting point, the hexabromide gave off hydrobromic acid in considerable amounts and slowly turned brown. At a temperature slightly over the melting point, the material gave off clouds of hydrobromic acid and the liquid turned dark brown. This experiment shows that the hexabromide is unstable at temperatures near its melting point and slowly loses hydrobromic acid. Since a melting point determination cannot be accurately taken by the capillary tube method, unless the rate of heating is comparatively slow, the correct melting point of hexabromide cannot be obtained by the ordinary method. Using pure hexabromide, a double bath, and a calibrated total immersion thermometer, melting points varying from 180.3° to 183° C. were obtained, depending upon the rate of heating; the lower value resulting when the rate of heating was slow, for example, a rise of one degree per minute.

Some linolic tetrabromide was prepared from the fatty acids of cottonseed oil. The melting point of the product was 112° to 113° C. A mixture of 95 per cent pure hexabromide and 5 per cent tetrabromide was dissolved in hot chloroform, the solvent evaporated, the solid material finely powdered and melting-point determinations made with a standardized total immersion thermometer, by the usual capillary method. The mixture melted at 176.5° to 177.2° C., while the pure hexabromide under the same conditions and same rate of heating melted at 181.8° to 182.3° C.

It is believed that this experiment explains the low melting point (177° C.) reported by Eibner for hexabromide, for the authors believe that in the Eibner method approximately 4 to 5 per cent of tetrabromide remains in the hexabromide precipitate. The criterion of purity of hexabromide in the Eibner method is freedom from yellow material. Since the tetrabromide is white and crystalline, it is easily seen that it would be possible for it to be present in the Eibner hexabromide. The fact that Eibner could not dry his product at 100° C. may also be explained by the presence of tetrabromide.

(*b*) *Bromine Content.* Some pure hexabromide, recrystallized from xylene, was analyzed for halogen content by a method, believed to be new, which depends upon the fact that the hexabromide when heated with 95 per cent alcohol and excess of zinc, quantitatively loses halogen, linolenic acid resulting, together with a small amount of the ethyl ester and the zinc salt of the linolenic acid. The removal of halogen by means of zinc to recover linolenic acid from the hexabromide is described by Erdmann and Bedford.[1] About half a gram of finely powdered pure hexabromide was weighed and heated in an Erlenmeyer flask under a reflux condenser with 30 to 40 cc. of 95 per cent alcohol and about 10 g. of 30-mesh powdered zinc. After about 30 min. the hexabromide entirely disappeared and the solution became clear. It was then boiled for about 1 hr. longer, filtered through a folded filter, and the zinc washed three times with hot alcohol and twice with hot distilled water. The filtrate was then titrated by the regular Volhard method, as described by Scott.[2]

Results on pure hexabromide:

63.04 per cent bromine
63.14 per cent bromine

Theoretical for hexabromide ($C_{18}H_{30}O_2Br_6$), 63.27 per cent bromine.

Some hexabromide from regular hexabromide determinations was also analyzed for bromine content by the method given above.

Results on hexabromide from determinations:

62.8 per cent bromine
62.6 per cent bromine

The determination of the bromine content is practically useless as a criterion of purity of the hexabromide, since the impurity which is the most difficult to remove, the tetrabromide of linolic acid, has such a high bromine content as to make the lowering of the percentage of bromine, due to the presence of small amounts of this impurity, so small that it lies within the limit of error in the bromine determination. This may be shown by the following calculations:

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[1] *Ber.*, **42**, 1324.

[2] "Standard Methods of Chemical Analysis," 2nd Ed., p. 81.

Theoretical for hexabromide ($C_{18}H_{30}O_2Br_6$), 63.27 per cent bromine

Theoretical for tetrabromide ($C_{18}H_{32}O_2Br_4$), 53.28 per cent bromine

Assuming 1 per cent of tetrabromide to be present:

$$\begin{aligned} 0.99 \times 63.27 &= 62.64 \\ 0.01 \times 53.28 &= 00.53 \\ \hline & 63.17 \text{ per cent} \end{aligned}$$

The above shows that 1 per cent of tetrabromide would lower the bromine content from 63.27 per cent to 63.17 per cent. This lowering of 0.1 per cent is well within the limit of error in the bromine determination, so that even 5 per cent of tetrabromide, causing a lowering of 0.5 per cent in the bromine content, could hardly be detected.

(*c*) *Solubility in Ether and Ether-Oily Bromide Mixture.* The following procedure was employed to deter solubility of pure hexabromide in absolute ether: Absolute ether which had been distilled over bright sodium was shaken at room temperature at intervals with an excess of pure hexabromide (recrystallized twice from hot xylene and thoroughly washed each time with absolute ether) for 24 hrs. in a tightly corked bottle. The next day the mixture was maintained at 0° C. in an ice bath for 4 hrs. About 75 cc. of the solution were then rapidly filtered into a tared glass-stoppered weighing bottle and weighed. The weight of the ether solution divided by the specific gravity of ether at 0° C. gave the volume of ether solution. The ether was evaporated carefully on a hot plate and the weighing bottle dried to constant weight in an oven at 100° C., cooled, and weighed. The total weight of the hexabromide residue divided by the volume of the ether solution taken gave the solubility per cc. as 0.000261 g. Absolute ether was also saturated with pure hexabromide at 24.5° C. and filtered at this temperature; 76.6 cc. of the filtrate upon evaporation yielded 0.0434 g. residue, giving the solubility of hexabromide at this temperature as 0.000566 g. per cc.

In order to determine whether loss of hexabromide takes place in a determination through solution in a mixture of oily bromides and ether during the first treatment of the impure hexabromide with wash ether, the following experiment was carried out:

The oily residues obtained by the evaporation of ether from the first washings of previous hexabromide determinations were dissolved in a small amount of absolute ether and cooled to approximately —10° C. to cause separation of any hexabromide which might be present. The ether solution was filtered and evaporated, and the oily bromides were entirely freed from traces of solvent by heating at 60° C. in a vacuum for several hours.

A mixture of 0.4927 g. pure hexabromide and 1.763 g. of the above oily bromide (these are the approximate amounts of hexabromide and oily bromide found in a determination) was weighed into a centrifuge tube and washed in the usual way at 0° C. with four 20-cc. portions of ether saturated with hexabromide. The tube was then dried and weighed and 0.4978 g. of hexabromide was recovered.

This experiment indicates that no considerable amount of hexabromide is lost by solution in the mixture of ether and oily bromide during the washing of impure hexabromide. The slight increase in weight of the hexabromide in the experiment described above can be attributed to the fact that a small amount of oily bromide was not washed out.

IV—METHOD PROPOSED

From the experimental work described, the following procedure for the determination of the hexabromide yield of the fatty acids of linseed oil was developed:

A. PREPARATION OF REAGENTS—The following reagents are necessary:

(*1*) *Chloroform.* Shake ordinary U. S. P. chloroform with several portions of water to wash out all the alcohol. Dry the product with granulated anhydrous calcium chloride over night in order to remove all traces of water. Decant from the calcium chloride and distill. Add to the distillate 3 cc. of absolute ethyl alcohol for every 100 cc. of chloroform. Keep in a stoppered brown bottle.

(*2*) *Bromine Solution.* Mix one part by volume of C. P. bromine[1] with two parts by volume of chloroform prepared as above. This solution must be made up fresh each day because it deteriorates upon standing.

(*3*) *Wash Ether.* Shake ordinary ethyl ether with 10 per cent of its volume of ice-cold distilled water. Separate and repeat the washing three times. Dry the washed ether with fused calcium chloride over night. Decant the ether through a folded filter into another flask and add thin slices of sodium. Warm gently on a steam bath under a reflux condenser until the evolution of gas by action of the sodium has practically ceased and bits of freshly cut sodium remain bright in the ether. Distill the ether into a dry bottle and add an excess (at least 3 g. per liter) of finely powdered hexabromide[2] of the fatty acids of linseed oil, previously prepared.

Shake at intervals for 2 or 3 hrs. or allow the mixture to stand over night. Then place the bottle in ice water so that the ether solution will be at zero or not above 2° C. for 3 hrs. Decant the ether solution rapidly through a folded filter into a dry bottle and keep tightly corked in order to prevent loss of ether by evaporation.

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[1] The authors have observed that samples of bromine marked "C. P." often contain considerable amounts of nonvolatile material. All bromine which is used must be redistilled unless it is found that 5 g. leaves no weighable residue upon evaporation.

[2] If no hexabromide is on hand from previous determinations, it may be easily prepared as follows: In a centrifuge tube dissolve about 5 g. of the fatty acids of linseed oil in 15 to 20 cc. of chloroform. Place the tube in a freezing mixture and add slowly with shaking bromine solution until a slight red color is permanent. Add a few drops of amylene to take up excess of bromine. Whirl in a centrifuge until the precipitate has settled and then pour off the chloroform. Rub up the precipitate with 20 cc. of cold absolute ether, whirl in a centrifuge, and pour off the wash ether. Repeat the washing with 3 more 20-cc. portions of ether. After drying, the hexabromide is pure enough for the preparation of wash ether

(4) *Amylene.* This material may be purchased from the Eastman Kodak Company. It is one of the organic chemicals prepared in the laboratory of the University of Illinois. It may be prepared in small quantities from amyl alcohol by the method of Adams.[1]

B. PREPARATION OF THE FATTY ACIDS—Weigh approximately 50 g. of linseed oil, place in a 1$^1/_2$ liter Florence flask, and add 40 cc. sodium hydroxide solution (sp. gr. 1.4) and 40 cc. alcohol. Place the mixture on a steam bath and heat for about $^1/_2$ hour. Add 1 liter of hot distilled water and insert into the neck of the flask a 2-hole rubber stopper carrying a tube which projects into the flask so that its end is slightly above the liquid, and pass a stream of carbon dioxide through the tube into the flask. The soap mixture may then be heated to remove the alcohol, either over a free flame or on the steam bath. If the free flame is used, a capillary "boiler" must be placed in the liquid, otherwise the soap solution will bump badly. If excessive foaming takes place, the current of carbon dioxide should be increased until it is strong enough to break up the foam. If the solution is heated on the steam bath usually about 2 to 3 hrs. are required to remove the alcohol, while if it is boiled over a free flame, $^1/_2$ hr. is usually sufficient. After the alcohol has been removed, cool the soap solution and acidify with dilute hydrochloric acid (1 : 1). Insert a 3-hole rubber stopper, carrying two glass tubes arranged as for a wash bottle, leaving the third hole in the stopper open for an outlet for the carbon dioxide. The inlet tube should extend to just above the layer of fatty acids, and the outlet tube should extend to the bottom of the flask. It is essential that the outlet tube should not extend down more than an inch or two outside of the flask, otherwise siphoning would take place, causing the liquid to boil inside the tube.

Pass a stream of carbon dioxide through the system, and boil gently, using a capillary boiler to prevent bumping, until the layer of fatty acids is clear. Plug the hole in the stopper which acts as an outlet for the carbon dioxide. The lower layer will be forced out through the outlet tube by the pressure of the CO_2. In this manner remove as much water as possible without losing any of the fatty acids, then remove the stopper and add about 500 cc. of hot distilled water, shake thoroughly so that the fatty acids are well washed, allow the fatty acids to separate and siphon off the wash water as before. Repeat the washing until the wash water does not give an acid reaction with methyl orange. Before removing the last washing, boil gently until the fatty acid layer is clear. After the last washing, remove the stopper and suck up with a pipette the last few globules of water. Filter the hot, fatty acids through a folded filter under an evacuated bell jar and keep in a well-stoppered bottle.

C. PREPARATION OF HEXABROMIDES—Weigh accurately in a weighed centrifuge tube (approximately 6$^1/_2$ in. long by 1 in. in diameter) 1.00 g. (plus or minus 0.05 g.) of linseed fatty acids, prepared as given above. Dissolve in 10 cc. of chloroform (see A, 1, p. 57) and place the tube in a freezing mixture, as near —5° C. as possible, made by adding a little dilute hydrochloric acid to finely cracked ice. Add bromine solution from a burette at the rate of one or two drops per second, shaking the tube well during the addition. At first the bromine color will be rapidly discharged, but later the mixture will assume a permanent orange color which indicates a slight excess of bromine. For most fatty acids of linseed oil, about 1 cc. of the bromine solution will be found necessary to give the orange color. At this point run in rapidly 0.5 cc. more of the bromine solution, shake well, and allow the tube to stand in the ice mixture for 10 min. Remove the tube from the freezing bath and add amylene drop by drop with shaking until the bromine color has entirely disappeared. Usually five to six drops of amylene are sufficient, but a slight excess does no harm. The addition of bromine solution must never be done in direct sunlight.

Attach the tube to a good water vacuum pump (one which will indicate a pressure not greater than 40 mm. of mercury) by means of a new one-hole rubber stopper. Evaporate the chloroform in a vacuum, warming the tube in water at 50° to 60° C. to hasten evaporation. The tube must be constantly shaken to prevent bumping of the chloroform. Towards the end of the evaporation, when the contents of the tube become more viscous, rotate and tilt the tube so that the oil will flow about half-way up the sides and thus present more surface for evaporation. When practically all the chloroform has been evaporated, place the tube in a bath at 55° to 60° C. for 15 min., keeping the suction on.

Detach from the pump and place the tube in a bath of finely cracked ice and water. When the tube is cold, pour down its sides 20 cc. of cold wash ether. The wash ether should have been previously placed in four corked test tubes graduated at 20 cc. by a file mark and kept at 0° C. in an ice bath. Thoroughly stir and rub up the bromide mixture with a rod, breaking up all the lumps. Return the tube to the ice bath for 2 min. and then whirl in a centrifuge until the precipitate has settled into a hard cake and the supernatant liquid is clear. Return the tube to the ice bath for 2 min., and then pour off the wash ether, making sure that no solid material is lost. Repeat the washing of the hexabromide precipitate three times in exactly the same way, using three 20-cc. portions of ice-cold wash ether and rubbing up the precipitate thoroughly each time. Use a weighed stirring rod and wash the precipitate adhering to the rod into the tube with the wash ether at each washing of the hexabromide. Afterwards dry and weigh the rod plus the slight coating of precipitate and add the weight of material on the rod to the weight of the main portion of hexabromide. After the fourth ether washing has been poured off, carefully incline and tap the tube and spread the hexabromide precipitate part way up the sides. Warm the tube in water at 50° to 60° C. until most of the ether has evaporated. Attach to the suction pump and place the tube in a bath at 60° to 70° C. for 15 min. Detach the tube from the pump, cool in cold water to room temperature, wipe dry with a towel and weigh at once. Dry the tube to constant weight in an oven at 100° to 110° C. The total weight of the precipitate times 100 divided by the weight of fatty acids taken, gives the hexabromide percentage. The hexabromide should be pure white when dry.

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[1] *J. Am. Chem. Soc.*, **40** (1918), 1950.

Special precautions should be taken as follows:

(1) Have the chloroform dry and adjust its alcohol content to 3 per cent.

(2) Make sure that all the chloroform is evaporated from the impure hexabromide before adding wash ether. This will be accomplished if the water pump indicates a pressure not greater than 30 to 40 mm. and the tube is heated in the bath at 60° C. for two-thirds of its length.

(3) Make sure that the wash ether is anhydrous and free from alcohol and that it is saturated with hexabromide at 0° C. Unless the wash ether is allowed to stand at 0° C. for a sufficient length of time before filtering off excess hexabromide, it will be supersaturated at 0° C. and will give high results. Care should be taken to prevent appreciable loss of ether by evaporation; it is well to cool the stock bottle of wash ether on hot days before uncorking.

(4) Make sure that the centrifuge tube containing hexabromide and the wash ether are kept as near 0° C. as possible during the process of washing. The finely cracked ice should be replenished at intervals.

V—RESULTS OBTAINED BY NEW METHOD

A. LINSEED OIL—See Table I.

TABLE I—RESULTS OBTAINED BY NEW HEXABROMIDE METHOD
(Values are expressed in percentage yields of hexabromide, calculated on the weight of fatty acids taken)

	Iodine Number =							
Analyst	181	182	183	186	191	184	182	185
A......	45.9	....	....	....	....	....	....	....
	46.3	....	....	....	46.2	....	....	....
	45.9	....	....	....	....	....	....	....
B......	46.3	....	....	....	....	....	....	....
	46.1	....	....	....	....	....	....	....
	46.1	46.1	....	46.9	46.7	46.1	46.2	....
	46.6	....	....	....	46.1	....	....	....
	46.1	....	....	....	....	....	....	....
	46.4	....	....	....	....	....	....	....
C......	45.6	....	....	....	....	....	....	....
D......	45.8	....	....	....	....	....	....	....
	45.6	....	45.9	....	....	....	....	....
	46.3	....	....	....	....	....	....	....
E......	45.7	....	....	....	....	45.7	45.9	46.8
						46.1	45.8	46.9
F......	45.6	....	....	....	....	....	....	....
G......	46.5	....	....	....	....	....	....	....

Up to the present time analytical results have been obtained on eight different linseed oils and are given in the table above. The sample of oil with iodine number of 181 was of known purity and results of seven different analysts working independently on this oil are given.

B. OTHER OILS—Samples of cottonseed oil and tung oil gave no visible amounts of hexabromide by the new method.

A sample of soy bean oil yielded 2.2 per cent hexabromide by the new method.

C. MIXTURES OF LINSEED AND OTHER OILS—A mixture of 80 per cent raw linseed oil (average hexabromide yield 46 per cent) and 20 per cent soy bean oil (average hexabromide yield 2.2 per cent) gave an average hexabromide yield by the new method of 36.6 per cent. The following simple calculation gives the theoretical value which would be expected:

$$\begin{aligned} 46 \times 0.80 &= 36.80 \\ 2.2 \times 0.20 &= 0.44 \\ \hline &\ 37.24 \text{ per cent (Theoretical)} \end{aligned}$$

A mixture of 95 per cent raw linseed oil (average hexabromide yield 46 per cent) and 5 per cent soy bean oil (average hexabromide yield 2.2 per cent) gave an average hexabromide yield by the new method of 44.1 per cent. The following simple calculation gives the theoretical value to be expected for the mixture:

$$\begin{aligned} 46.0 \times 0.95 &= 43.7 \\ 2.2 \times 0.05 &= 0.1 \\ \hline &\ 43.8 \text{ per cent (Theoretical)} \end{aligned}$$

A mixture of 75.6 per cent raw linseed oil (average hexabromide yield 46 per cent) and 24.4 per cent tung oil (hexabromide yield nil) gave an average hexabromide yield by the new method of 32.1 per cent.

$$46 \times 75.6 = 34.8 \text{ per cent (Theoretical)}$$

The results of hexabromide tests by the new method on mixtures of linseed oil with other oils indicate, it is believed, that it may be possible to detect as little as 5 per cent adulteration of linseed oil with oils low in hexabromide yield.

All determinations of hexabromide yield of linseed oils examined so far in this laboratory have fallen between the values 45.6 per cent and 46.9 per cent. If further investigations show that the hexabromide yield of pure raw linseed oil is a more constant value than the iodine number, it may be possible to make a quantitative determination in adulterated samples of linseed oil of the content of oils like soy bean oil, that give low hexabromide yields.

VI—SUMMARY

Various published methods for the determination of the hexabromide yield of linseed oils have been investigated, especially the Eibner method. An explanation is given of the observed fact that this method does not yield concordant results. Experimental work leading to the development of a new hexabromide method is given, the main features of which are the addition of bromine to the fatty acids of linseed oil in a solvent in which the resulting hexabromide is soluble, the addition of a reagent to remove excess bromine, the removal of the solvent by evaporation, and the isolation of the hexabromide free from contaminating bromides by thorough washing with absolute ether saturated with hexabromide. A table of results, obtained by the new method, is given, showing concordancy between several analysts working independently. The results obtained so far indicate that the hexabromide yield of pure raw linseed oil is a more constant value than the iodine number. Results are also given on mixtures of linseed and other oils, such as soy bean oil, which indicate that it may be possible to estimate quantitatively adulteration of linseed oil with other oils which give a low hexabromide yield.

THE ANALYTICAL CHEMISTRY OF URANIUM AND ITS SEPARATION FROM OTHER RARE ELEMENTS[1]

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Received July 28, 1919

The analytical chemistry of uranium has received a considerable amount of attention. The accuracy of the various known methods for its determination is in very few instances as satisfactory as might be desired and the problem deserves further study. In the following paper the more common methods have been critically reviewed and additions have been made to the determination as well as to the separation of uranium from other elements with which it is associated.

PRECIPITATION OF URANIUM BY MEANS OF AMMONIUM HYDROXIDE

This method is one of the oldest and in pure uranium solutions it is frequently convenient. The uranium is precipitated as ammonium uranate which is converted by ignition to the green oxide U_3O_8. An alternate procedure is to heat either the green oxide or ammonium uranate to UO_2 in a current of dry hydrogen. Zimmermann[2] claimed that the weight of U_3O_8 was not constant unless it had been ignited in an atmosphere of oxygen. Kern[3] showed that the reduction of U_3O_8 to UO_2 by hydrogen is unreliable. He considered that the reduction gave better results when made in platinum crucibles than when conducted in porcelain and attributed this to the ready passage of gases through the platinum.

EXPERIMENTAL—Portions of a standard solution of uranium nitrate were diluted to a volume of 200 cc. with water. Ammonium hydroxide was added and the solution containing the precipitate was then boiled for 15 min. The precipitate was filtered and washed with a 2 per cent solution of ammonium nitrate, dried and ignited in a porcelain crucible.

Table I

Sample	U_3O_8 Present	U_3O_8 Found	Error
1	0.2303	0.2300	—0.0003
2	0.2303	0.2304	+0.0001
3	0.2303	0.2303	0.0000
4	0.2303	0.2305	+0.0002
5	0.2303	0.2304	+0.0001

PRECIPITATION OF URANIUM AS PHOSPHATE

This method was first suggested by Leconte[4] and later worked out by Pisani,[5] who precipitated the uranium as uranyl hydrogen phosphate with alkali phosphate. When disodium hydrogen phosphate is used the precipitate is difficult to filter and to wash free from sodium. Kern[6] used ammonium dihydrogen phosphate as a precipitant and claimed that the uranyl ammonium phosphate could be made pulverulent and crystalline by boiling for half an hour. He found the precipitate to be as easily handled as that of ammonium uranate. Brearley[1] modified the method by using microcosmic salt in the presence of sodium thiosulfate and obtained a precipitate easy to filter and wash, but difficult to ignite to constant weight on account of its hygroscopic character.

EXPERIMENTAL—In following the procedure of Kern the difficulties encountered were the tendency of the precipitate to pass through the filter paper and the hygroscopic character of the uranyl pyrophosphate. The precipitate absorbed moisture more rapidly than lime.

Table II

Sample	U_3O_8 Present	$(UO_2)_2P_2O_7$ Calculated	$(UO_2)_2P_2O_7$ Found	Error
1	0.2303	0.2928	0.2932	+0.0004
2	0.2303	0.2928	0.2932	+0.0004
3	0.2303	0.2928	0.2936	+0.0008
4	0.2303	0.2928	0.2935	+0.0007
5	0.2303	0.2928	0.2934	+0.0006
6	0.2303	0.2928	0.2925	—0.0003

PRECIPITATION OF URANIUM BY MEANS OF YELLOW AMMONIUM SULFIDE

Ammonium sulfide has been recommended as a means of separating uranium from the alkalies and alkaline earths and also, when mixed with ammonium carbonate, from the metals whose sulfides are insoluble in the mixture. Berthier[2] was apparently the first to use this reagent in the determination of uranium. Rose[3] used ammonium polysulfide as a precipitating agent for uranium. Remele[4] finds that uranium sulfide is somewhat soluble in ammonium polysulfide and recommends boiling the solution from 30 min. to one hour. Winkler[5] compared the ammonium sulfide with the ammonium hydroxide method and pronounced it reliable.

EXPERIMENTAL—The procedure of Remele was followed for the most part. To a hot solution of uranyl nitrate, slightly acid with acetic acid, a slight excess of freshly prepared ammonium polysulfide was added and the solution boiled for one hour. As soon as the precipitate settled the solution was filtered hot and the precipitate washed with a hot 2 per cent solution of ammonium nitrate, dried and ignited to U_3O_8. The precipitate formed in this way settles quickly as a black granular powder, but the residue on ignition is somewhat darker than that obtained when ammonium uranate is ignited.

Table III

Sample	U_3O_8 Present	Residue Found	Error
1	0.2486	0.2512	+0.0026
2	0.2486	0.2517	+0.0031
3	0.2486	0.2511	+0.0025
4	0.2486	0.2514	+0.0028
5	0.2486	0.2515	+0.0029
6	0.2303	0.2333	+0.0030
7	0.2303	0.2324	+0.0021
8	0.2303	0.2330	+0.0027
9	0.2303	0.2321	+0.0018
10	0.2303	0.2319	+0.0016
11	0.2303	0.2326	+0.0023

The results are high, but no amount of heating at the highest temperature obtainable with a good Meker burner would lower them in the least. The residues when dissolved in nitric acid and tested with barium chloride showed sulfate in every case, indicating that a portion of the sulfur present had been oxidized to sulfate during the ignition.

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[1] Presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

[2] *Ann.*, **213** (1882), 316.

[3] *J. Am. Chem. Soc.*, **23** (1901), 702.

[4] *Repertoire de Pharmacie*, **9** (1853), 361.

[5] *Compt rend.*, **62** (1861), 72.

[6] *J. Am. Chem. Soc* **23** (1901), 708.

[1] "The Analytical Chemistry of Uranium," Longmans, Green & Company.

[2] *Ann.*, **46** (1843), 184.

[3] *Pogg. Ann.*, **116** (1862), 352.

[4] *Z. anal. Chem.*, **4** (1865), 379.

[5] *Chem. News*, **43** (1881), 153.

VOLUMETRIC DETERMINATION OF URANIUM BY POTASSIUM PERMANGANATE

Belchoubeck[1] suggested the use of permanganate for the volumetric determination of uranium. Guyard[2] criticized this method because of the over-reduction of the uranium. Zimmermann[3] reduced uranyl sulfate to uranous sulfate by means of zinc. He carried out the reduction in a closed flask and poured the reduced solution into a dish or beaker before titrating. Under these conditions he found definite reduction corresponding to a valence of four.

Kern[3] repeated Zimmermann's work and found no over-reduction, but obtained satisfactory results when he reduced uranyl sulfate by passing the solution through a Jones reductor containing an 18-inch column of 20-mesh amalgamated zinc. He allowed the reduced solution to fall through the air on to a small funnel and then into a receiving flask which contained about 1 g. of sodium carbonate. In this way oxidation in the flask is prevented. While his results show excellent agreement, he states that the reduction could not be carried further by passing the solution twice through the reductor.

Pulman[4] obtained quite different results from those of Kern. He found that it required more than 20 min. to pass the same volume of solution that Kern had used, and that when the solution was drawn into a receiver containing dry sodium carbonate there was always an over-reduction. He thought that the over-reduction could be corrected by pouring the reduced solution through the air into a beaker before titrating.

TABLE IV

SAMPLE	Time of Reduction Min.	U_3O_8 Taken	U_3O_8 Found
1	30	0.2486	0.2998
2	20	0.2486	0.3333
3	15	0.2486	0.2970
4	15	0.2486	0.2870
5	40	0.2486	0.2825
6	30	0.2486	0.3070
7	15	0.2486	0.3034
8	25	0.2486	0.3062
9	20	0.2303	0.2687
10	30	0.2303	0.2730
11	60	0.2303	0.2598
12	35	0.2303	0.2730
13	30	0.2303	0.2758
14	20	0.2303	0.2828

EXPERIMENTAL—In our experiments the details of Kern's method were slightly modified. The Jones reductor contained 20-mesh amalgamated zinc in a column 15 in. long and $^7/_8$ in. in diameter. The reductor was connected with a suction flask containing 1 g. of sodium carbonate. 150 cc. of uranyl sulfate solution containing 1 part of sulfuric acid to 6 parts of water were used. The reductor was filled with a hot solution of 1 : 6 sulfuric acid in order to furnish acid for decomposing the sodium carbonate in the receiving flask and to maintain the acid concentration of the uranyl sulfate. The hot solution of uranyl sulfate was drawn through the reductor by gentle suction and the reductor washed out, first with warm 1 : 6 sulfuric acid, followed by enough hot water to make the total volume in the receiving flask 500 cc. The reduced solution was immediately titrated in the receiving flask.

The high results obtained indicate that the reductions were carried out below the tetravalent state. This was also evidenced by the color of the reduced solution which was always red-brown instead of the characteristic green color of uranous sulfate. The results agree with those of Pulman in that it required 15 min. and longer to draw 150 cc. of the solution through the reductor and that there was always an over-reduction. The results in the table below were obtained by following the Pulman procedure of pouring the reduced solution through the air into a beaker before titrating.

TABLE V

SAMPLE	Time of Reduction Min.	Number of Times Poured	U_3O_8 Taken	U_3O_8 Found
1	20	1	0.2303	0.2704
2	30	1	0.2303	0.2670
3	45	1 slowly	0.2303	0.2431
4	30	1 slowly	0.2303	0.2457
5	20	2	0.2303	0.2323
6	20	2	0.2303	0.2332
7	24	1	0.2303	0.2546
8	25	1 slowly	0.2303	0.2340
9	25	4 rapidly	0.2303	0.2329
10	20	6	0.2303	0.2316
11	15	8	0.2303	0.2316
12	15	5	0.2303	0.2316
13	25	6	0.2490	0.2440
14	25	5	0.2490	0.2457
15	30	4	0.2490	0.2502
16	25	4	0,2490	0.2502
17	15	5	0.2490	0.2505
18	20	5	0.2490	0.2507

A similar series of experiments using a much weaker solution of permanganate to minimize the error, and filtering the solutions through glass wool, resulted in the same order of error shown in the results in Table V.

EXTENT OF OVER-REDUCTION

A series of experiments was carried out to ascertain whether this over-reduction was really definite. The reduction apparatus was modified so that a known excess of permanganate could be added to the reduced solution without allowing the solution to come in contact with the air. The receiving flask was fitted with a four-holed rubber stopper carrying a Jones reductor, a dropping funnel and inlet and outlet tubes. Carbon dioxide was passed through the entire system until the air was completely removed. The reduction of the uranyl sulfate was carried out as usual and the reduced solution collected in an atmosphere of carbon dioxide, after which an excess of permanganate was introduced through the dropping funnel. An excess of permanganate, back-titrated with a standard sodium oxalate solution, was added.

TABLE VI

SAMPLE	Time of Reduction Min.	Strength of Acid	Volume at Titration Cc.	U_3O_8 Taken	U_3O_8 Found
1	20	1 : 6	500	0.2518	0.2716
2	20	1 : 6	500	0.2518	0.2792
3	25	1 : 6	500	0.2518	0.2946
4	27	1 : 6	500	0.2518	0.2757
5	25	1 : 6	500	0.2518	0.2840
6	12	1 : 6	500	0.2518	0.3162

From the above data it can be concluded that the reduction goes below the uranous condition, but in no case had it reached the valence of three. The varying results obtained under conditions as nearly alike as possible indicate the futility of trying to obtain a definite over-reduction by the Jones reductor.

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[1] *Z. anal. Chem.*, **6** (1867), 120.

[2] *Bull. soc. chim.*, **1** (1864), 93.

[3] *Loc. cit.*

[4] *Am. J. Sci.*, **166** (1903), 229.

ACTION OF OTHER REDUCING AGENTS ON URANYL SOLUTIONS

MAGNESIUM—While the mechanical difficulties with metallic magnesium are considerable, due to its tendency to float, when these are overcome by anchoring the magnesium in a substantial manner, the metal when treated with an acid uranyl solution always gives over-reduction.

SODIUM AMALGAM proved entirely unsatisfactory.

ORGANIC REDUCING AGENTS such as formaldehyde, acetaldehyde and acetone gave either no reduction or only a very slight one.

PHOTOGRAPHIC DEVELOPERS, such as hydroquinone, dianol, metaquinone, metol, and elon are without reducing action on uranyl sulfate either in acid or alkaline solution,

HYDROXYLAMINE showed varying amounts of reduction while hydrazine gave no reduction.

SEPARATION OF URANIUM FROM VANADIUM

Friedel and Cumenge[1] separated uranium from vanadium by evaporating the nitric acid solution of these metals to dryness with an excess of nitric acid and extracting the uranyl nitrate from the residue with a warm dilute solution of ammonium nitrate. Hillebrand[2] failed to extract all the uranium from such a residue by this reagent because of the occlusion of uranyl nitrate in the vanadic oxide.

Kern[3] states that A. C. Langmuir used mercuric oxide and mercurous nitrate successfully for separating vanadium from uranium by precipitating vanadium as mercurous vanadate and determining the uranium in the filtrate after removing the excess of mercury with hydrogen sulfide. This process seems questionable since Alibegoff[4] precipitated uranium with mercuric oxide in separating it from the alkalies and alkaline earths.

Fritchle[5] precipitated uranium from vanadium by sodium hydroxide in the presence of sodium carbonate. This method is open to criticism, as uranium is not entirely precipitated by sodium hydroxide in the presence of alkaline carbonates.

In 1842 Peligot[6] found that uranyl nitrate dissolved readily in ether and used this reagent in the purification of uranium from pitchblende. This procedure suggests a process for separating uranium from other metals.

EXPERIMENTAL—The apparatus used was the usual form of Soxhlet extraction apparatus with the paper thimble commonly used with volatile solvents. In preliminary experiments on the solubility of uranyl nitrate in anhydrous ether it was noted that when a solution of uranyl nitrate is evaporated to dryness at water-bath temperature, a portion of the dried residue is insoluble in ether. This behavior of uranyl nitrate when heated to 100° has been observed by Lebeau,[1] who found that at this temperature it was partially dissociated into $UO_3.H_2O$ and nitric acid. Because of this decomposition it was necessary to moisten the evaporated residue with nitric acid in the experiments that follow.

The method adopted was to evaporate a solution of uranyl nitrate, sodium vanadate and nitric acid in a glass boat of convenient size for placing in the extraction thimble. The dried residue was moistened with 5 cc. of nitric acid added in two portions, the first at the beginning of the extraction and the second after the ether had siphoned over three times.

TABLE VII

SAMPLE	U_3O_8 Present	V_2O_5 Present	U_3O_8 Found	ERROR
1........	0.2996	0.1000	0.2989	—0.0007
2........	0.2996	0.1000	0.2983	—0.0013
3........	0.2996	0.1000	0.2993	—0.0003
4........	0.2996	0.1000	0.2986	—0.0010
5........	0.2996	0.1000	0.2982	—0.0014
6........	0.2996	0.1000	0.3005	+0.0009
7........	0.2996	0.1000	0.2993	—0.0003
8........	0.2996	0.1000	0.2992	—0.0004
9........	0.2996	0.1000	0.3005	+0.0009
10........	0.2996	0.1000	0.2998	+0.0002
11........	0.2996	0.1000	0.2998	+0.0002
12........	0.2996	0.1000	0.2995	+0.0001
13........	0.2996	0.1000	0.2995	+0.0001

SEPARATION OF URANIUM FROM MOLYBDENUM

Uranyl nitrate can be extracted from molybdenum trioxide and ammonium nitrate by treating with ether the residue obtained by evaporating to dryness a mixture of uranyl nitrate, ammonium molybdate and nitric acid. The extraction of the uranium from the molybdenum trioxide is made in exactly the same manner as the separation of uranyl nitrate from vanadium pentoxide.

TABLE VIII

SAMPLE	MoO_3 Present	U_3O_8 Present	U_3O_8 Found	ERROR
1	0.1000	0.2490	0.2494	+0.0004
2........	0.1000	0.2490	0.2484	—0.0006
3........	0.1000	0.2490	0.2493	+0.0003
4........	0.1000	0.2490	0.2488	—0.0002
5........	0.1000	0.2490	0.2490	0.0000
6........	0.1000	0.2490	0.2483	—0.0007
7........	0.1000	0.2490	0.2488	—0.0002
8........	0.1000	0.2490	0.2486	—0.0004
9........	0.1000	0.2490	0.2481	—0.0009

SEPARATION OF URANIUM FROM TUNGSTEN

When a mixture of uranyl nitrate, sodium tungstate and nitric acid is evaporated to dryness, the tungsten appears in the form of tungstic trioxide, WO_3. On extracting such a residue with anhydrous ether a quantitative separation of uranium from tungsten can be made. The extraction is carried out in exactly the same way as previously indicated in the separation of uranium from vanadium.

SEPARATION OF URANIUM FROM VANADIUM BY MEANS OF GLACIAL ACETIC ACID

Among the numerous organic solvents for uranyl nitrate, glacial acetic acid is one of the best. This reagent has no apparent solvent action on vanadium pentoxide. Preliminary experiments showed that the residue left by the evaporation of an aqueous solution of uranyl nitrate is only partially soluble in glacial acetic acid. The uranyl nitrate dissolved readily in the acetic acid but the uranium oxide formed by the partial hydrolysis of the uranyl nitrate is not dissolved by the reagent. It does become soluble, however, when moistened with nitric acid.

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[1] *Bull. soc. chim.*, [3] **21** (1899), 328.

[2] *Am. J. Sci.*, **10** (1900), 135.

[3] *Loc. cit.*

[4] *Ann.*, **233** (1886), 133.

[5] *Chem. News*, **82** (1900), 258.

[6] *Ann. chim. phys.*, [3] **5** (1842), 1.

[1] *Bull. soc. chim.*, [4] **11** (1912), 737.

TABLE IX

		U_3O_8		
SAMPLE	WO_3 Present	Present	Found	ERROR
1........	0.1580	0.2507	0.2504	—0.0003
2........	0.1580	0.2507	0.2509	+0.0002
3........	0.1580	0.2507	0.2506	—0.0001
4........	0.1580	0.2507	0.2505	—0.0002
5........	0.1580	0.2507	0.2501	—0.0006
6........	0.1580	0.2507	0.2503	—0.0004
7........	0.1580	0.2507	0.2501	—0.0006
8........	0.1580	0.2507	0.2504	—0.0003

Vanadium pentoxide, formed by evaporation to dryness of a solution of sodium *m*-vanadate with nitric acid, was found to be insoluble in cold or in hot glacial acetic acid.

A solution of acetic acid of 90 per cent strength by volume, hot or cold, was found to have no solvent action on vanadium pentoxide. The same strength of acid mixed with a trace of nitric acid shows no solvent action on V_2O_5.

Eighty per cent acetic acid either hot or cold does not dissolve vanadium pentoxide, but mixed with nitric acid (1.42) in the ratio of 1 part of nitric to 20 parts of 80 per cent acetic acid is without action when cold but shows a decided solvent action on V_2O_5 when boiled.

Sixty per cent acetic acid when cold does not dissolve vanadium pentoxide, but when warm extracts considerable amounts of V_2O_5.

Fifty per cent acetic acid, either hot or cold, dissolves considerable quantities of V_2O_5.

Acetic acid of 95 per cent strength or over, mixed with nitric acid (1.42) in the ratio of 1 part nitric to 20 parts acetic acid, is without solvent action on V_2O_5.

When a solution mixed with uranyl nitrate and sodium *m*-vanadate is evaporated with nitric acid (1.42) the residue can be extracted with glacial acetic acid to which a small amount of nitric acid has been added. It is recommended that for each 100 cc. of glacial acetic acid 5 cc. of 1.42 nitric acid be added.

TABLE X

		U_3O_8		
SAMPLE	V_2O_5 Present	Taken	Found	ERROR
1........	0.2000	0.2518	0.2516	—0.0002
2........	0.2000	0.2518	0.2522	+0.0004
3........	0.2000	0.2518	0.2519	+0.0001
4........	0.2000	0.2518	0.2517	—0.0001
5........	0.2000	0.2518	0.2516	—0.0002

This work was suggested by Dr. Victor Lenher and carried out under his direction. I take this opportunity to thank Dr. Lenher for his helpful suggestions and criticisms.

SQUALENE: A HIGHLY UNSATURATED HYDROCARBON IN SHARK LIVER OIL

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Received May 14, 1919

In a previous communication,[1] I have shown that two Japanese shark liver oils (Ai-zamé and Heratsuno-zamé) contain high proportions of a new highly unsaturated hydrocarbon of the formula $C_{30}H_{50}$, for which I have proposed the name "squalene." Thenceforth, I have examined a considerable number of Japanese shark liver oils, amounting to thirty-six species of the fish. The result of the investigations shows that squalene is a general constituent of certain shark liver oils; it has been found to occur far more frequently in the liver oils from the sharks belonging to the family *Squalidae*, but the oils from a few other sharks, notably those of the families *Cetorhinidae*, *Chlamydoselachidae*, *Dalatiidae*, and *Scylliorhinidae*, also contain the hydrocarbon. These oils have low specific gravities (usually below 0.9 at 15°/4° C.) and contain a high percentage of unsaponifiable matter which consists chiefly, if not totally, of squalene. On the other hand, the liver oils from many other sharks have higher specific gravities and less unsaponifiable matter; in them, squalene has not been detected. Although the sharks that give the liver oils containing squalene are not so abundant and rather limited in species, nevertheless their distribution appears to be very wide, inasmuch as some foreign *Squalidae* sharks have been confirmed to contain a hydrocarbon closely resembling and probably identical with squalene.

In the present paper which is a continuation of my previous report, are described my later investigations on Japanese shark liver oils in a somewhat similar way as in the former paper. The investigation of this interesting hydrocarbon is important from scientific as well as industrial points of view, and a rather lengthy description of the individual oils in the following pages, will not be unimportant, I believe.

There is very scant mention of shark liver oil in the literature. Recently A. C. Chapman[1] has published reports of investigations on "spinacene," a new hydrocarbon obtained from certain fish liver oils. The oil used for examination by Chapman was procured from Lisbon. The Portuguese shark liver oils, especially those obtained from the livers of *Centrophorus granulosus* and *Scymnus lichia*, have already been examined by H. Mastbaum,[2] who has reported the occurrence of hydrocarbons in these oils (although not proved by actual analysis), and from whom Chapman got information as to the origin of his sample. The hydrocarbon named spinacene by Chapman has the formula $C_{29}H_{48}$,[3] and forms bromine and hydrogen addition products of composition very similar to those of squalene. Although some of their physical constants differ a little, the similarity of the two hydrocarbons is remarkably great. Considering the fact that I have already prepared the hexahydrochloride of squalene of the formula $C_{30}H_{50}.6HCl$, which has properties very similar to spinacene hexahydrochloride, $C_{29}H_{48}.6HCl$, and also that spinacene has been obtained from an oil of the *Squalidae* sharks, it is highly probable that spinacene is identical with squalene.

EXAMINATION OF JAPANESE SHARK LIVER OILS FOR THE OCCURRENCE OF SQUALENE

The oils from thirty-six species of Japanese sharks have been examined.[4] As the commercial oils are not reliable for genuineness and also limited in species, the samples of the oils used for the examination were prepared from the fish, as far as circumstances permitted, in the laboratory under my supervision. Squalene was detected and confirmed by distilling the oils under diminished pressure, or by the formation of the characteristic hexahydrochloride. The isolation of unsaponifiable matters which are solid at ordinary temperatures was often sufficient confirmation of the absence of squalene. In the following descriptions of the oils the experimental details of the detection of squalene are omitted and the results only are mentioned.

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[1] THIS JOURNAL, 8 (1916), 889.

[1] *J. Chem. Soc., Trans.*, **1917**, 56, **1918**, 458.

[2] *Chem. Abs.*, **10** (1916), 285.

[3] In the first communication (*Loc. cit.*) Chapman gave the formula $C_{30}H_{50}$ for spinacene.

[4] The total species of sharks found in Japan are reported to be more than sixty in number.

As the specific gravity of shark liver oils is an important indication of their properties, more especially of the occurrence of squalene, I have classified them in the following two groups, according as the specific gravity is lower or higher than 0.9 at 15° 4° C. The oils are described according to the ascending order of specific gravity.

I—SHARK LIVER OILS OF LOW SPECIFIC GRAVITY

All the shark liver oils of this group contained squalene. The oils of lower specific gravity contained more squalene than the higher, although some exceptions were observed. Besides squalene, these oils appeared to contain some unknown alcohols in notable amount. Larger by far in numbers, the oils from the sharks of the family *Squalidae* belonged to this group, as has already been remarked in the previous report.

(1) AI-ZAMÉ OIL—This oil has been described in my previous report. By later examination of the shark, this fish was found not to be "*Squalus mitsukurii*," but "*Centrophorus sp.*," the exact species being still unknown. Of all the shark liver oils examined, Ai-zamé oil had the lowest specific gravity and saponification value, and at the same time the highest iodine value and refractive index; the content of unsaponifiable matter was also the highest. The highest content of squalene accounts for these abnormal properties of the oil. The oil contained 82 to 85 per cent of the hydrocarbon.

(2) IMORI-ZAMÉ OIL—This shark, also known by the name of Shusu-zamé in Japan, is a fish belonging to the family *Scylliorhinidae*. Its scientific name is *Pristiurus pilosus* (Garman). A sample of the fish caught in the sea near Province Izu was used as the material for examination, January 1918. This fish (male) was 48.5 cm. in length (measured from tip of snout to root of upper lobe of caudal) and weighed 1057 g. The color of the fish was dark brownish gray on the back, becoming lighter on the under side. It had no spines. The liver was yellowish white and weighed 256 g. The weight of the oil obtained by heating the chopped liver was 215 g., *i. e.*, about 84 per cent by weight of the liver. Naturally the residue contained still an appreciable amount of the oil. The oil was a pale yellow liquid which deposited no stearine even in the winter seasons.

Imori-zamé oil had very low specific gravity and saponification value, and very high iodine value and refractive index. The content of unsaponifiable matter was also very high. This oil contained about 80 per cent of squalene. The oil is, therefore, next to Ai-zamé oil in its high content of the hydrocarbon. It is interesting to note that Imori-zamé does not belong to the family *Squalidae*.

(3) HERATSUNO-ZAMÉ OIL—This was also described in the previous report. It is to be remarked that this oil contained besides squalene a hydrocarbon probably of the composition $C_{20}H_{38}$.

(4) FRILL-SHARK OIL—Frill-shark (Japanese: Rabuka-zamé), *Chlamydoselachus anguineus* (Garman), is of the deep waters of the Sagami Sea, and was first studied by the American ichthyologist, Samuel Garman. It has the form of primitive sharks and is known to be a sole living representative of the family *Chlamydoselachidae*. The following two samples were examined:

Frill-shark Oil No. 1—This was obtained from a female fish caught in the Sagami Sea, March 1918. Body length, 96 cm.; length of tail, 28 cm.; total length, 124 cm. The pinkish white liver weighed 545 g., from which 370 g. (68 per cent) of the oil were obtained. The oil was a pale yellow liquid and at 15° C. was filled with a fine crystalline precipitate.

Frill-shark Oil No. 2—This female fish was also caught in the Sagami Sea, May 1918. Total length, 167 cm.; body weight, about 10 kg.; the liver (pinkish gray-white) weighed 2583 g., from which 1600 g. (about 62 per cent) of the oil were obtained. This oil was a light orange-yellow liquid.

Although frill-shark liver oil had low specific gravity and high content of unsaponifiable matter, the iodine value and refractive index were comparatively low. The oil really contained squalene but the percentage of the hydrocarbon was low (less than 7 per cent). The main constituents of the oil appear to be esters of some unknown alcohols.

(5) MOMIJI-ZAMÉ OIL—This oil was obtained from Momiji-zamé, *Lepidorhinus foliaceus* (Günther), a shark of the family *Squalidae*. A male fish procured from Misaki in Province Sagami, January 1917, was 38 cm. in length and weighed 281 g. The liver weighed 49 g., from which 34 g. (69.4 per cent) of the oil were obtained by heating. The oil was a pale yellow liquid of a peculiar odor.

(6) TSUMAGURO SAGAMI-ZAMÉ OIL—This was obtained from the liver of a squaloid shark, *Centrophorus atromarginatus* (Garman), caught in the Sagami Sea, February 1918. The fish (female) had a body length of 49 cm. and weighed 1120 g. The grayish white liver weighed 177 g.; the oil obtained was about 100 g., *i. e.*, 56.5 per cent of the liver. The oil was pale yellow in color and deposited a small quantity of stearine in winter.

(7) BIRODO-ZAMÉ OIL—Birodo-zamé, *Zameus squamulosus* (Gunther), is a shark also of the family *Squalidae* and is rather common in the deep waters of the Sagami and Suruga Seas. It has a rough-scaled skin of a violet-black color, hence this shark is usually called "Kuro-zamé" (black shark) in Japan. Of five samples of the oil examined, the following two are mentioned here:

Birodo-zamé Oil No. 1—A female fish caught in the Sagami Sea was procured from Odawara, a city in

Province Sagami, May 1915. It was about 86.5 cm. in length and weighed 10.4 kg. The grayish white liver was very large and weighed 2545 g. By heating, (melting method), 1955 g. (76.8 per cent) of the oil were obtained from the liver. The oil was a clear, pale yellow liquid of a characteristic and not unpleasant odor.

Birodo-zamé Oil No. 2—A male fish from the Suruga Sea (May 1915) was used. The length of the body of the fish was about 75 cm., the weight being about 4.5 kg. The liver was grayish white and weighed 1044 g. The yield of the oil was 822 g. (78.7 per cent). The oil resembled oil No. 1 very closely.

(8) TARŌ-ZAMÉ OIL—Tarō-zamé, *Centrophorus acus* (Garman), belongs to the same genus *Centrophorus* of the family *Squalidae* as Ai-zamé and Tsumaguro sagami-zamé. A female fish caught at Misaki in Province Sagami was procured from the Tokyo Fish Market, December 1917. It had a body length of 37 cm. and weighed 370 g. The liver had a milky white color and weighed 78 g. 53 g. of the oil were obtained by heating the chopped liver to about 100° C.; the residue was then extracted with ether, by which 9 g. of the oil were recovered; the total yield of the oil, therefore, 62 g., was 79.2 per cent by weight of the liver. The weight of the residue was only 4 g.

The oil obtained by the melting method was a pale yellow liquid which deposited a small quantity of a granular mass at 3° C. This oil contained more than 40 per cent of squalene.

(9) KINBEI-ZAMÉ OIL—This shark is a new species belonging to the genus *Lepidorhinus* of the family *Squalidae*, and the very fish used for the present experiment was the first specimen that has ever been found. The Japanese name "Kinbei-zamé" and the scientific name "*Lepidorhinus kinbei*" have been given to the fish by Mr. Shigeho Tanaka, of the College of Science, Imperial University of Tokyo. The fish was caught in the Sagami Sea and procured from the Tokyo Fish Market, January 1918. The fish (female) had a dark violet-brown skin and somewhat resembled Birodo-zamé in its outer appearance. It had a total length of 140 cm. and weighed 18.75 kg. It was pregnant with 12 eggs. The liver had a yellowish white color and weighed 4463 g. (23.8 per cent of the total weight), from which 3507 g. (78.5 per cent of the liver weight) of the oil were obtained by the melting method.

The oil was a pale yellow liquid of little odor and taste. Its properties resembled those of Birodo-zamé oil. The content of squalene was about 30 per cent.

(10) KANATSUBO-ZAMÉ OIL—This oil was obtained from Kanatsubo-zamé or Yoroi-zamé, *Dalatias licha* (Bonnaterre), a shark belonging to the family *Dalatiidae*.[1] The fish resembles some of the squaloid sharks, but it has no spine. The sample of the oil was prepared from the liver of a Kanatsubo-zamé from Odawara in Province Sagami, January 1918. The fish was said to have had a body length of 1.5 m. The liver was yellowish gray-white and weighed 5140 g. By the melting method 4185 g. (81.5 per cent) of the oil were obtained.

The oil had a pale yellow color and did not deposit stearine in the winter seasons. Its properties resembled those of Kinbei-zamé oil, but the iodine value and refractive index were a little lower. The oil contained about 30 per cent of squalene.

(11) YUME-ZAMÉ OIL—This oil was obtained from *Centroscymnus owstonii* (Garman) (*Squalidae*) caught in the Suruga Sea, November 1915. This shark (male?) resembled Birodo-zamé very closely. It was about 65 cm. in length and weighed 2.86 kg. The grayish white liver weighed 835 g., from which 650 g. (78 per cent) of the oil were obtained. The oil resembled Birodo-zamé oil and contained about 24 per cent of squalene.

(12) KUROKO-ZAMÉ OIL—The name "Kuroko-zamé" is somewhat ambiguous, differing in species according to locality. Samples of Kuroko-zamé were obtained from Miyagi Prefecture, April 1917. The fish were ascertained to be *Centroscyllium ritteri* (Jordan and Fowler), belonging to the family *Squalidae*. The following five fish were procured:

No.	Sex	Length Cm.	Weight G.	Weight of Liver G.
1	Female	36	607	175
2	Female	35	484	122
3	Female	37	468	111
4	Female	37	622	158
5	Male	34.5	429	94

The livers were very large and of a grayish white color. From the total weight of 660 g. of liver, 420 g. (63.6 per cent) of the oil were obtained. The oil was a light yellow liquid; it solidified at —10° C. This sample of Kuroko-zamé oil differed greatly in its properties from the oil examined by me some twelve years ago.

(13) BASKING-SHARK OIL—Basking-shark (Japanese: Uba-zamé), *Cetorhinus maximus* (Gunner), (*Cetorhinidae*) is the largest of all living sharks. It is an animal of arctic seas, but is occasionally found off the coast of Japan. The following three samples of the oil were examined:

Basking-shark Oil No. 1—This oil was procured from the Yokohama Fish Oil Company. The place of its production is not known. It was an orange-yellow liquid having a somewhat unpleasant odor.

Basking-shark Oil No. 2—This oil was also procured from the above-mentioned company under the name of "Baka-zamé" oil, June 1915.[1] It was reported to be prepared in Province Hidachi. The oil resembled the Oil 1. This sample of basking-shark oil contained saturated hydrocarbons, the main constituent of which has already been identified to be some iso-octadecane, $C_{18}H_{38}$.[2]

Basking-shark Oil No. 3—Oil prepared in Province Suruga. A pale yellow oil of slightly fishy odor.

Basking-shark liver oil contained more than 20 per cent of squalene.

II—SHARK LIVER OILS OF HIGH SPECIFIC GRAVITY

The shark liver oils of this group, with the exception of Higezuno, crow-shark, and Fujikujira oils, did not contain squalene. But the first group contained notable amounts of unsaponifiable matter, which appeared to consist of some unknown alcohols. The last members, on the other hand, contained only comparatively small amounts of unsaponifiable matter and their properties resembled those of ray liver oils.

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[1] *Scymnus lichia* described by Chapman (*Loc. cit.*) appears to be identical with *Dalatias licha*. The fish then belongs to the *Dalatiidae* and not to the *Spinacidae* or *Squalidae*.

[1] "Baka-zamé" means literally "foolish shark"

[2] THIS JOURNAL, 9 (1917), 1098.

(14) HIGEZUNO OIL—This oil was obtained from the liver of Higezuno, *Cirrhigaleus barbifer* (Tanaka), a barbel-bearing shark belonging to the family *Squalidae*. The oil sample was prepared from the liver of a fish bought at the Tokyo Fish Market, April 1918. The fish (female) had a body length of about one meter. The liver, which was milky-white with yellow and red shadings, weighed 2677 g. and was very rich in oil. By the melting method 2268 g. (85 per cent by weight of the liver) of the oil were obtained. The oil was an orange-yellow liquid with a peculiar odor common to shark liver oil. The specific gravity (0.9009) of this oil was nearly on the boundary between the two classes of shark liver oils; its low iodine value was also characteristic. On passing HCl into a well-cooled ethereal solution of the oil, about 0.3 per cent of a crystalline precipitate was obtained; so the oil probably contained a small proportion of squalene. The chief constituents of the unsaponifiable matter (28.76 per cent) appeared to be some unknown alcohols.

(15) CROW-SHARK OIL—Crow-shark (Japanese: Karasu-zamé), *Etmopterus frontimaculatus* (Pietschmann), is a deep-water species belonging to the *Squalidae*. It is one of the smallest of sharks and is luminous in the dark. The samples of crow-shark were obtained from Misaki in Province Sagami, December 1916. The fish were reported to have been angled from water of some 300 to 400 fathoms deep in the Sagami Sea. The total number of the fish was 10. They had body lengths of 18 to 24.5 cm. and weighed 40 to 93 g. The skin of the fish was brownish black; the spines in the dorsals were sharp and comparatively large. The pinkish gray livers were found to be very small, their total weight being only 42 g. against a total weight of 583 g. of the fish. The oil was prepared by heating the chopped livers to about 90° C. and then extracting them with petroleum ether. The yield was 12.5 g., or 29.8 per cent by weight of the liver.

The oil was a pale orange-yellow colored liquid which deposited a little stearine in winter, and contained a small percentage (less than 10 per cent) of squalene.

(16) FUJIKUJIRA OIL—Fujikujira, *Etmopterus lucifer* (Jordan and Snyder), is a shark closely resembling a crow-shark. It also belongs to the *Squalidae* and, like a crow-shark, is a small deep-water fish and luminous. The samples of Fujikujira were obtained from Misaki, October 1916. The total number was 9; body lengths, 18 to 30 cm.; weights, 31 to 192 g. The total weight of the fish was 665 g. The livers were dark gray and weighed 105 g. The oil was prepared in the same way as crow-shark oil. The yield was 50 g., or 47.6 per cent of the liver.

The oil was a pale yellow liquid. In winter, it deposited a little stearine. This oil had the same specific gravity as crow-shark oil and contained a very small percentage of squalene.

(17) ONDEN-ZAMÉ OIL—Onden-zamé, *Somniosus microcephalus* (Bloch and Schneider), (*Somniosidae*), is probably identical with the sleeper-shark, nurse, or Greenland shark, and also with "Eishai," *Laemargus microcephalus*, described by H. Bull.[1] This shark is found in the Arctic Seas, south to Cape Cod, Oregon, France, and Japan. The body of the fish is thick and clumsy, sharply tapering behind. The sample of the oil used for the examination was prepared from the liver of an Onden-zamé caught in the Suruga Sea, February 1918. The fish was reported to have had a body length of about 2 meters and weighed about 56 kg. The liver received was about a half of the whole and weighed 2500 g. From 1000 g. of the liver, 605 g. of the oil were obtained by the melting method. The oil was a yellow liquid which remained clear even in winter. In spite of the high content of unsaponifiable matter squalene was not detected in this oil.

(18) HOKKAIDŌ ABURA-ZAMÉ OIL—The exact species of this shark has not yet been ascertained, but it appears to be either *Squalus mitsukurii* or *Squalus sucklii*. Of the four samples of the oil examined, the writer mentions two:

Hokkaidō Abura-zamé Oil No. 1—This oil was prepared from the liver of a female fish which had been bought in Hokkaidō, April 1915. The fish had a dark gray skin and had spines in the dorsals. The body length was about 90 cm., the weight about 6.07 kg. The liver weighed 594 g. and gave 350 g. (59 per cent by weight of the liver) of the oil by heating the chopped materials to about 100° C. in a porcelain basin. The oil was a yellow liquid of a peculiar odor and when rubbed on the skin, a fishy smell was noticed.

Hokkaidō Abura-zamé Oil No. 2—This oil was prepared from the liver of a fish which had also been bought in Hokkaido. The total weight of the livers was 550 g., from which 306 g. (55.7 per cent) of the oil were obtained in the same way as in the case of Oil 1. This oil resembled Oil 1 in its outer appearance.

Although Hokkaidō Abura-zamé oil contained a rather high percentage of unsaponifiable matter, squalene was not detected in it. The sterol-free unsaponifiable matter obtained from Oil 2 was a yellow, crystalline semi-solid of 34° C. m. p. By elementary analysis it was found to consist of 79.98 per cent C, 11.71 per cent H, and 8.31 per cent O. Its hydrogenation product, prepared by means of platinum black as catalyzer, was a white crystalline solid which after two recrystallizations melted at 66° to 67° C. No further study of the substance has been made, but it seems likely that the unsaponifiable matter consisted of some alcohols.[2]

(19) KAGURA-ZAMÉ OIL—Kagura-zamé, *Hexanchus corinus* (Jordan and Gilbert), (*Hexanchidae*), is a large shark with six gill-openings. The sample fish was procured from Odawara in Province Sagami, April 1918. It was 2.1 m. in length and weighed 61 kg. The liver (grayish white with reddish yellow

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[1] Benedikt-Ulzer, "Analyse der Fette und Wachsarten," **1908**, 913.

[2] It will be an important and interesting investigation to ascertain the compositions of unknown alcohols which occur so frequently and largely in shark liver oils.

shadings) weighed 10.5 kg., from 1000 g. of which 627 g. of the oil were obtained by the melting method. The oil was an orange-yellow liquid; at the ordinary temperatures it deposited stearine.

(20) NAGAHERA-ZAMÉ OIL—Nagahera-zamé, *Scylliorhinus macrorhynchus* (Tanaka), belongs to the family *Scylliorhinidae*. Three fish caught in the sea near Izu were used January 1918. The lengths of the fish were 50 to 65 cm. and the weights 257 to 635 g. From a total weight of 100 g. of the livers about 50 g., or 50 per cent, of oil were obtained. The oil had a light yellow-orange color and solidified in winter.

(21) BLUE-SHARK OIL—Blue-shark or mackerel shark (Japanese: Ao-zamé), *Isuropsis glauca* (Müller and Henle), is one of the well-known ferocious sharks. It swims about seas to attack fish shoals, and has been known to devour men. Its appearance resembles mackerel with an indigo-blue skin on the back. The fish is found in Japan chiefly in the northern and northeastern seas.

The sample of the oil was prepared from the liver of a blue-shark bought at the Tokyo Fish Market, April 1915. The fish had a body length of about 1.5 m. The pink-white liver weighed 1921 g., from which 469 g. of the oil (24.4 per cent of the liver) were obtained by the melting method. It was a yellow liquid which deposited a large amount of stearine at the ordinary temperatures. The oil contained only a small amount of unsaponifiable matter; its iodine value was also far lower than those of the other shark liver oils.

(22) TOGARI-TSUNO-ZAMÉ OIL—Togari-tsuno-zamé, *Squalus japonicus* (Ishikawa), resembles Hokkaidō Abura-zamé. A female fish was procured from the Tokyo Fish Market, February 1916. It was 95.5 cm. in length and weighed 9.45 kg. The fish was found to be pregnant with nine well-matured foeti. The following two oils were prepared:

Liver Oil No. 1 from the Mother Fish—The gray liver weighed 937 g. The oil was obtained by the usual way of heating. The yield was 414 g. or 43.7 per cent of the liver. The oil was a yellow liquid; at 10° C. a small quantity of stearine was deposited.

Liver Oil No. 2 from the Foeti—The foeti had body lengths of 22–25 cm. The oil was obtained from four of them. The total weight of the four foeti was 439 g.; the weight of their livers was 51 g. The oil obtained was 23 g. or about 45 per cent of the liver. The oil was a pale yellow liquid, closely resembling the former oil, but it did not deposit stearine at 10° C.

The results of the determination of the constants, etc., of the oils have shown that the foetus oil had higher specific gravity, iodine value, and refractive index, while the contents of the unsaponifiable matter were nearly equal. In spite of the fact that the shark belongs to the family *Squalidae*, squalene was not present in the oils.

(23) ABURA-ZAMÉ OIL—This oil was obtained from Abura-zamé, *Heptranchias deani* (Jordan and Starks) (*Hexanchidae*). The fish lives in the southern seas of Japan. Unlike other sharks, it has seven gill-openings. Two oils were examined:

Abura-zamé Oil No. 1—The fish used was procured from the Tokyo Fish Market, March 1917. Body length, 32.5 cm.; weight, 279 g. The liver (yellowish gray-white) weighed only 16 g., from which 4.7 g. (29.4 per cent) of the oil were extracted with petroleum ether. The oil was a light orange-yellow liquid of a characteristic odor.

Abura-zamé Oil No. 2—This sample was also procured from the Tokyo Fish Market, April 1917. Body length, about 80 cm.; weight, about 5.6 kg. The liver was a light pinkish gray-white and weighed 789 g. By the melting method 427 g. (54.1 per cent) of the oil were obtained. The oil content of the liver of this fish was far greater than that of Fish 1. The oil was a pale yellow liquid which at the ordinary temperatures deposited some stearine.

(24) DOCHI-ZAMÉ OIL—Dochi-zamé or Yamori, *Triakis scyllium* (Müller and Henle) (*Galeidae*), is chiefly found in the southwestern seas of Japan. A sample of the shark was procured from the Tokyo Fish Market, April 1917. Body length, 48 cm.; weight, 820 g.; weight of liver (grayish brown), 48 g. The oil extracted from the liver with petroleum ether was 8 g. (16.7 per cent). The oil was of a yellowish orange color and deposited a somewhat large amount of stearine.

(25) MEJIRO-ZAMÉ OIL—Mejiro-zamé, Wani-zamé, or *Shirafuka* (white-shark), *Carcharhinus japonicus* (Temminck and Schlegel), is also found chiefly in the southern seas of Japan. The oil was prepared from the liver of a Mejiro-zamé procured from the Tokyo Fish Market, April 1917. The original fish (female) had a body length of 144 cm. and a weight of 42.7 kg. The liver was brownish gray and weighed 1.88 kg. From 936 g. of the liver, 128 g. of the oil were obtained by the melting method. As the content of the oil in the liver was rather small, the separation of it from the residue was difficult and so the yield was poor. The oil was yellow and deposited a large amount of stearine.

(26) NANUKA-ZAMÉ OIL—This oil was obtained from Nanuka-zamé, *Cephaloscyllium umbratile* (Jordan and Fowler), a shark belonging to the family *Scylliorhinidae*. The fish used (December 1917) for examination had a body length of 103 cm. and a weight of about 6.8 kg. The liver was yellowish gray-white and weighed 950 g. By melting, 516 g. (54.5 per cent) of the oil were obtained. The oil was light yellow and deposited a somewhat large amount of stearine in winter.

(27) THRESHER-SHARK OIL—The liver of a thresher-shark (Japanese: Onaga-zamé), *Alopias vulpes* (Gmelin), caught in the sea near Province Awa, was used for the experiment, December 1917. The original fish was reported to have had a total length of 3.5 meters and a weight of 25 kg. The liver received was not the whole of it and weighed 730 g. It was pinkish gray in color. By melting, only 50 g. of the oil were obtained owing to the difficulty of separating it from the residue. The oil was an orange-yellow liquid which deposited a large amount of stearine at 8° C

TABLE I—SHARK LIVER OILS OF LOW SPECIFIC GRAVITY

LIVER OIL FROM	Sp. Gr. (15°/ 4° C.)	Acid Value	Sapon. Value	Iodine Value (Wijs)	Ref. Ind. (20° C.)	Unsapon. Matter Per cent	M. P. of Fatty Acids Deg. C.	Fatty Acid Polybromides Per cent (Solvent: Ether)	Br Content of Polybromides Per cent	Color Reaction with H_2SO_4	Squalene Approximate Percentage
(1) Ai-zamé (No 1)	0.8644	0	23.0	344.6	1.4930	90.2	...	16.6	...	Reddish violet	84.8
Ai-zamé (No 2)	0.8662	0.1	28.2	330.4	1.4925	87.3	...	....	...	Yellowish brown	82.4
(2) Imori-zamé	0.8664	0.3	28.1	309.0	1.4912	85.5	...	7.0	...	Brown with faint reddish violet	79.4
(3) Heratsuno-zamé	0.8721	0.5	52.5	261.7	1.4850	72.9	...	2.3	...	Violet-red	58.3
(4) Frill-shark (No. 1)	0.8749	0.6	93.4	134.4	1.4716	51.7	...	4.8	...	Violet-red	7.1
Frill-shark (No. 2)	0.8885	0.5	115.8	130.3	1.4725	37.1	...	5.6	69.85	Violet-red	....
(5) Momiji-zamé	0.8842	0.4	73.5	207.2	1.4850	62.7	31	14.0	...	Brown	....
(6) Tsumaguro sagami-zamé	0.8845	0.5	81.5	236.6	1.4845	58.3	...	....	...	Brown with violet-red	....
(7) Birodo-zamé (No. 1)	0.8939	0.3	106.6	205.1	1.4808	43.6	...	....	...	Violet-red	27.6
Birodo-zamé (No. 2)	0.8925	0.3	106.6	155.7	1.4762	43.7	28–29	7.1	70.02	Violet-red	19.5
(8) Tarō-zamé	0.8866	1.1	71.6	233.5	1.4869	62.9	31–33	29.0	70.58	Light violet	....
(9) Kinbei-zamé	0.8884	0.7	92.7	215.1	1.4817	51.3	27–29	15.4	70.01	....	30.3
(10) Kanatsubo-zamé	0.8890	0.2	98.1	191.5	1.4791	48.5	25–27	9.6	69.77	Orange-red	29.9
(11) Yume-zamé	0.8926	0.4	107.2	172.4	1.4790	46.3	...	....	...	Dirty violet-red	24.3
(12) Kuroko-zamé	0.8979	0.5	120.4	149.0	1.4758	36.9	29–30	17.4	69.82	Violet-red	13.5
(13) Basking-shark (No. 1)	0.8969	4.3	109.4	161.8	1.4772	48.4	30	3.1	...	....	26.0
Basking-shark (No. 2)	0.8839	1.1	102.5	178.3	1.4773	41.9	...	....	...	....	....
Basking-shark (No. 3)	0.8859	0.9	86.0	191.8	1.4815	55.5	...	....	...	....	....

(28) GAIKOTSU-ZAMÉ OIL—This oil was obtained from Gaikotsu-zamé or Gobō-zamé, *Pristiurus eastmani* (Jordan and Snyder) (*Scylliorhinidae*), which lives in the southern seas of Japan. The fish (male) used was procured from Misaki, Province Sagami, January 1917. It had a body length of 45 cm.; weighed 539 g. The liver was grayish yellow and weighed 41 g., from which 14 g. (34.2 per cent) of the oil were obtained. The oil was a light yellow liquid which deposited a small amount of stearine in winter. Although this shark belongs to the same genus as Imori-zamé, the properties of the oil are very different from those of the oil from the latter.

(29) YOSHIKIRI-ZAMÉ OIL — This shark, *Prionace glaucus* (L.), belongs to the same family (*Galeidae*) as Mejiro-zamé and like the latter is one of the large sharks. The sample was procured from the Tokyo Fish Market, February 1917. It had a body length of about 2 m. The liver was dark gray and weighed 3.6 kg. By the melting method, 678 g. (18.8 per cent) of the oil were obtained from the liver. The difficulty of separating the oil from the residue was similar to the case of Mejiro-zamé. The oil was an orange-yellow liquid and deposited stearine in winter.

(30) SAW-SHARK OIL—Saw-shark (Japanese: Nokogiri-zamé), *Pristiophorus japonicus* (Günther) (*Pristiophoridae*), is one of the well-known sharks. The sample of oil was obtained from the liver of a saw-shark procured from the Tokyo Fish Market, April 1915. The fish had a total length of about 83 cm. and weighed about 2.2 kg. The liver (light pinkish gray-white) weighed 154 g., from which 41 g. (27 per cent) of the oil were obtained by melting. The oil was a light yellow liquid. It deposited only a small quantity of stearine.

(31) PORBEAGLE OIL—This oil was obtained from the liver of a porbeagle (Japanese: Nezumi-zamé, literally meaning "rat-shark"), *Lamna cornubica* (Gmelin) (*Lamnidae*), a large shark resembling the blue shark. The fish is called Kato-zamé in Hokkaidō, Japan, and is found abundantly on the Pacific coast of the island. The sample of the oil was prepared from the liver of a porbeagle caught in the sea near Mito, Province Hidachi, April 1915. The liver received was not the whole but about three-fourths. Nevertheless, it weighed about 12 kg., and was of a pinkish gray-white color. By melting method, 5.1 kg. (about 42 per cent) of the oil were obtained from it. The oil was an orange-yellow liquid with a little deposit of stearine.

(32) HOSHI-ZAMÉ OIL—This oil was obtained from the liver of *Cynias manazo* (Bleeker) (*Galeidae*). The sample of the fish was procured from the Tokyo Fish Market, February 1915. The fish (female) was of about 76 cm. in length and weighed about 1760 g. The grayish yellow liver weighed 108 g., from which 33 g. (30.6 per cent) of the oil were obtained by extraction with ether. The oil was a bright yellow liquid which at 10° C. deposited a large amount of stearine.

(33) CAT-SHARK OIL—This oil was obtained from the liver of a cat-shark, *Heterodontus japonicus* (Duméril), procured from the Tokyo Fish Market, February 1915. It had a body length of about 38 cm. and weighed 750 g. The liver was brownish yellow and weighed only 50 g. By extracting with ether, 13 g. (26 per cent) of the oil were obtained. The oil was an orange-yellow liquid with an unpleasant odor; at 10° C. it deposited a large amount of stearine.

(34) TIGER-SHARK OIL—Tiger-shark (Japanese: Tora-zamé) is a fish of the family *Scylliorhinidae*. Its scientific name is *Halaelurus torazame* (Tanaka). The sample used for experiment was procured from Hokkaidō, April 1918. The total number of the fish received was 24 (13 male and 11 female). The lengths of the fish were 43 to 49 cm., the weight varying from 310 to 463 g.; the total weight amounted to 9316 g. The livers were yellowish gray to dark brownish gray, with sometimes blue or green shadings. They were small in size, the weight varying from 14.5 to 44.5 g. From the total weight of 753.5 g. of the liver, about 200 g. (26.6 per cent) of the oil were obtained by the melting method. The oil was a yellow-orange liquid which deposited a small amount of stearine.

(35) HAMMER-HEADED-SHARK OIL—The sample of oil from the liver of this well-known shark (*Sphyrna zygaena*) was obtained from a hammer-headed-shark caught in the Suruga Sea, April 1915. It was a reddish yellow liquid of an unpleasant odor.

(36) ANGEL-FISH OIL—Angel-fish (Japanese: Kasuzamé), *Squatina japonica* (Bleeker) (*Squatinidae*), resembles the rays in the flat appearance of the body. The two following samples were examined:

Angel-fish Oil No. 1—This oil was obtained from an

TABLE II—SHARK LIVER OILS OF HIGH SPECIFIC GRAVITY

LIVER OIL FROM	Sp. Gr. (15°/4° C.)	Acid Value	Sapon. Value	Iodine Value (Wijs)	Ref. Ind. (20° C.)	Unsapon. Matter Per cent	M. P. of Fatty Acids Deg. C.	Fatty Acids Poly-bromides Per cent (Solvent: Ether)	Br Content of Poly-bromides Per cent	Color Reaction with H_2SO_4	Squalene Approximate Percentage
(14) Higezuno	0.9009	0.4	131.7	91.3	1.4702	28.8	32–33	6.8	68.88	Light violet-red	Small quantity
(15) Crow-shark	0.9079	0.9	146.0	116.2	1.4750	24.1	29.3	20.3	70.77	Violet-red	....
(16) Fujikujira	0.9079	1.1	147.3	104.7	1.4724	23.2	.....	....	.....	Violet-red	Small quantity
(17) Onden-zamé	0.9099	0.5	149.2	107.3	1.4740	16.2	.....	13.6	69.81	Deep violet	Not present
(18) Hokkaidō Abura-zamé (No. 1)	0.9105	2.3	159.6	100.5	1.4729	12.0	.....	....	.....	Deep violet	Not present
Hokkaidō Abura-zamé (No. 2)	0.9128	2.3	156.7	120.5	1.4748	17.0	29.5–30.5	23.6	69.14	Deep violet	Not present
(19) Kagura-zamé	0.9146	0.5	165.7	124.5	1.4740	14.4	.....	26.3	.....	Light violet-red	Not present
(20) Nagahera-zamé	0.9161	0.9	178.8	103.1	1.4725	1.5	26–27	17.2	.....	Brown with violet-red	Not present
(21) Blue-shark	0.9178	0.5	179.8	109.3	1.4741	1.7	30	25.7	70.32	Violet-red	Not present
(22) Togari-tsuno-zamé (No. 1)	0.9182	1.1	164.8	141.4	1.4775	10.4	28–29	38.4	68.92	....	Not present
Togari-tsuno-zamé (No. 2)	0.9254	0.8	166.5	183.9	1.4842	10.9	32–33	62.9	68.53	....	Not present
(23) Abura-zamé (No. 1)	0.9208	1.0	165.8	166.3	1.4795	9.8	31	58.2	71.16	....	Not present
Abura-zamé (No. 2)	0.9162	0.4	174.9	118.5	1.4734	12.7	.....	....	.....	Violet-red	Not present
(24) Dochi-zamé	0.9245	1.7	185.7	143.7	1.4778	6.1	.....	....	.....	Violet-red	Not present
(25) Mejiro-zamé	0.9246	0.3	182.7	126.9	1.4775	5.0	33–33.5	30.4	70.20	Violet	Not present
(26) Nanuka-zamé	0.9255	0.4	182.9	143.1	1.4780	1.4	33–34	49.4	70.28	Light violet-red	Not present
(27) Thresher-shark	0.9261	1.5	183.9	139.6	1.4786	2.0	.....	....	.....	Violet-red	Not present
(28) Gaikotsu-zamé	0.9262	2.4	184.5	131.6	1.4772	2.4	.....	....	.....	Violet-red	Not present
(29) Yoshikiri-zamé	0.9276	1.0	172.7	160.8	1.4841	8.4	32–33	41.2	69.92	Deep violet	Not present
(30) Saw-shark	0.9285	1.3	182.2	170.5	1.4809	4.1	31–32	51.5	70.29	Violet-red	Not present
(31) Porbeagle	0.9286	0.3	177.0	181.2	1.4829	3.6	27–28	64.0	71.30	Reddish violet	Not present
(32) Hoshi-zamé	0.9267	0.4	181.6	183.7	1.4808	2.9	31–32	65.8	71.25	....	Not present
(33) Cat-shark	0.9305	1.2	178.5	138.5	1.4781	3.9	.....	....	.....	....	Not present
(34) Tiger-shark	0.9308	2.6	183.3	197.9	1.4845	0.9	.....	....	.....	Dirty violet-red	Not present
(35) Hammer-headed-shark	0.9312	2.4	179.8	199.7	1.4849	1.7	31	66.7	70.56	....	Not present
(36) Angel-fish (No. 1)	0.9311	0.4	184.6	191.1	1.4823	1.9	34–35	72.3	71.43	Violet-red	Not present
Angel-fish (No. 2)	0.9322	1.0	182.4	197.3	1.4833	2.5	.....	....	.....	Violet-red	Not present

angel-fish procured from the Tokyo Fish Market, April 1917. The fish (female) had a body length of 93 cm. and weighed 8.6 kg. The liver was of three-pronged form, yellowish gray with red shadings; its weight was 315 g. By extracting with petroleum ether, 84 g. (26.7 per cent) of the oil were obtained. The oil was a yellow-orange liquid; at the ordinary temperatures it deposited a somewhat large amount of stearine. The odor of the oil was unpleasant and fishy.

Angel-fish Oil No. 2—This oil was obtained from the liver of an angel-fish (male) also procured from the Tokyo Fish Market, April 1917. The fish was 88.7 cm. in length and weighed 6.75 kg. The liver weighed 156 g., from which 28 g. (17.9 per cent) of the oil were obtained by extracting with petroleum ether. It will be seen that the weight and oil-content of the liver of this male fish were far smaller than those of the female fish above described. The oil resembled Oil 1, but the amount of stearine deposited was smaller.

Angel-fish liver oil had the highest specific gravity of all the shark liver oils examined by me. Not only the outer appearance but also the properties of the oil resembled those of ray liver oils.

PROPERTIES OF SQUALENE AND SOME OF ITS DERIVATIVES

In the previous report,[1] a few properties of squalene and some of its derivatives have been described. The following are the results of further experiments:

SPECIFIC GRAVITY—Squalene obtained from Aizamé oil No. 2 gave sp. gr. at 15°/4° C. 0.8591 and at 20°/4° C. 0.8559.

VISCOSITY—The specific viscosity determined by Ostwald's viscosimeter as compared to water at the same temperature was as follows: at 15° C., 14.3; at 25° C., 12.2.

The time of flow of 50 cc. of squalene determined by Redwood's viscosimeter was 91 seconds at 15° C. and 73 seconds at 25° C.

DRYING PROPERTIES—About 0.5 g. of squalene was dropped on to a thin layer of about 10 g. of Livache's lead powder spread on a large watch glass and the whole was kept in a light room for about one month (temperature 7.5° to 22° C.). The increase of weight, or the oxygen absorption of squalene, observed during this interval was as follows:

Days	Oxygen Absorption Per cent	Days	Oxygen Absorption Per cent
1	3.9	7	21.3
2	7.1	12	22.0
3	13.4	23	24.0
4	20.3	28	24.3
5	20.8		

The remarkable increase of weight was observed on the fourth to fifth days; the increase thereafter was slow and it became nearly constant on the twenty-third to twenty-eighth days. The oxygen absorption calculated from the formula $C_{30}H_{50}O_6$ is 23.66 per cent.

DEBROMINATION OF THE BROMINE ADDITIVE COMPOUND OF SQUALENE—By treating squalene dodecabromide, $C_{30}H_{50}Br_{12}$, with glacial acetic acid and zinc dust on a water bath for 2 hrs., an orange-yellow oily liquid of the refractive index 1.4950 at 20° C. was obtained. Judging from the refractive index it is probable that squalene was regenerated, but the yield was rather poor, only amounting to about 35 per cent of the theoretical. The difficulty of debromination was similar to the case of the polybromides of fish oil fatty acids.

SQUALENE HEXAHYDROCHLORIDE[1]—Hydrogen chloride is readily absorbed by squalene with the formation of the most characteristic hexahydrochloride. Ten g. of squalene were dissolved in 50 cc. of dry ether. To the solution well cooled with ice and snow, dry hydrogen chloride was passed. On saturation the color of the solution changed to pinkish and on standing a crystalline precipitate was obtained with a yield of about 5 g. It was refined by recrystallization from acetone. The analysis of the compound gave the following results:

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[1] *Loc. cit.*

[1] According to a recent investigation of A. C. Chapman (*J. Chem. Soc Trans.*, **1918**, 458), the percentage of Cl in spinacene hexahydrochloride is stated to increase on repeated recrystallizations from benzene and alcohol. With the view of ascertaining whether such increase of Cl content occurred in the case of squalene hexahydrochloride, the writer recrystallized it four times from acetone. The results of the analysis of the refined product were as follows:

0.2249 substance gave 0.3047 AgCl (Carius method)
0.1990 substance gave 0.2705 AgCl (Carius method)
Cl = 33.50, 33.61 per cent.

Thus, the results were practically identical with the above-mentioned.

0.1707 substance gave 0.3590 CO_2, 0.1387 H_2O
0.1671 substance gave 0.2243 AgCl (Carius method)
0.2372 substance gave 0.3215 AgCl (Carius method)
0.3570 substance gave 0.4840 AgCl (Baubigny and Chavanne method)
C = 57.35 per cent, H = 9.09 per cent, Cl = 33.20, 33.53, 33.54 per cent
$C_{30}H_{50}.6HCl$ requires C = 57.22 per cent, H = 8.96 per cent, Cl = 33.82 per cent

The substance was, therefore, confirmed to be squalene hexahydrochloride.

Squalene hexahydrochloride recrystallized from acetone forms white, lustrous laminae. It begins to sinter at about 112° C. and melts at about 125° C.; at the same time decomposition occurs evolving hydrogen chloride. It is difficulty soluble in ether, petroleum ether, and alcohol in the cold; hot absolute alcohol dissolves it. It is soluble in warm carbon tetrachloride and glacial acetic acid, and in cold chloroform. It is readily soluble in hot acetone, but on cooling, nearly the whole of it is deposited as crystals, so that acetone is one of the best solvents for refining this compound by crystallization. In the preparation of this compound acetone may be substituted for ether as the solvent for squalene.

The hexahydrochloride is obtained directly from original shark liver oil by dissolving it in ether or acetone and saturating the solution with dry hydrogen chloride in the cold.

Cod liver oil gives no insoluble hydrochloride by the same treatment, but on adding one per cent of squalene to the oil, an appreciable white precipitate is formed; with 5 per cent, a distinct precipitate is obtained. The formation of the compound serves, therefore, as a most delicate test for the detection of squalene.

SQUALENE HEXAHYDROBROMIDE—Squalene forms a hexahydrobromide similar to the hexahydrochloride. Hydrogen bromide was passed into a well-cooled solution of 2 g. of squalene in 10 cc. of ether. On saturation a copious white precipitate was obtained together with a small quantity of an oily substance. The yield of the precipitate was about 3 g. It was well washed with ether and recrystallized from acetone.

0.1717 substance gave 0.2532 CO_2, 0.0980 H_2O
0.2259 substance gave 0.2813 AgBr (Carius method)
0.1720 substance gave 0.2162 AgBr (Carius method)
C = 40.22 per cent, H = 6.39 per cent, Br = 52.99, 53.48 per cent
$C_{30}H_{50}.6HBr$ requires C = 40.18 per cent, H = 6.30 per cent, Br = 53.52 per cent

Squalene hexahydrobromide is a white, crystalline substance of silky luster. When heated in a capillary tube it turns brown at 115° to 118° C. (The coloration is probably due to the vapor of bromine formed by decomposition.) The coloration then gradually disappears and the substance finally melts to a clear liquid at 125° to 126° C.

SQUALENE HEXAHYDROIODIDE—This compound is formed in the same way as the other two halogen halides, but it is rather unstable and somewhat difficult to obtain in pure state.

When dry hydrogen iodide was passed into a well-cooled ethereal (20 per cent) solution of squalene, the liquid at first became somewhat turbid, then a brownish red insoluble liquid compound was formed, the supernatant liquid becoming clear. Then a large quantity of white crystals were deposited, the upper liquid now changing to orange-yellow. On standing over one night the colored lower liquid disappeared and the colorless solution was filled with white crystalline precipitates. The yield of the precipitate was about 2 g. from 2 g. of squalene. This crude product was recrystallized from a small quantity of ethyl acetate. The refined product formed pure white crystals, but the yield was very poor. When acetone was used as solvent the solution turned brownish red and no crystals were obtained. The analysis of the compound confirmed it to be squalene hexahydroiodide as follows:

0.1648 substance gave 0.1856 CO_2, 0.0732 H_2O
0.1156 substance gave 0.1370 AgI (Carius method)
C = 30.71 per cent, H = 4.98 per cent, I = 64.04 per cent
$C_{30}H_{50}.6HI$ requires C = 30.56 per cent, H = 4.79 per cent, I = 64.65 per cent

The hexahydroiodide sinters at about 105° C. and melts at 108° to 109° C. to a pink liquid.

DECHLORINATION OF SQUALENE HEXAHYDROCHLORIDE—It has already been mentioned that hydrogen chloride is evolved on heating squalene hexahydrochloride to its melting point. In the present experiment acetic acid and zinc dust were used for the elimination of chlorine.

20 g. of the hexahydrochloride, 200 g. of glacial acetic acid, and 100 g. of zinc dust were heated in a flask on a water bath for 2 hrs. in a current of carbon dioxide. The white crystals of the hexahydrochloride gradually disappeared and an oily layer was formed on the surface of the liquid. The contents of the flask were removed to a separating funnel, diluted with water, and shaken with ether. The ether layer was then washed successively with aqueous NaOH solution and water, dehydrated with anhydrous Na_2SO_4, and finally the ether was evaporated off. The residue obtained was a nearly colorless, oily substance of sp. gr. 0.9065 at 15°/4° C., and refractive index 1.4930 at 20° C. 10 g. of this substance were heated under 4.5 mm. pressure; it boiled at 252° to 254° C. giving 9 g. of the distillate, a colorless, viscous oily liquid. It had the sp. gr. (15°/4° C.) 0.8995, (20°/4° C.) 0.8958, the refractive index (20° C.) 1.4938, and the iodine value 281. It was, therefore, nearly identical with the original substance and appeared to be a pure chemical compound. The elementary analysis gave the following results:

0.1820 substance gave 0.5410 CO_2, 0.1913 H_2O
C = 81.07 per cent, H = 11.77 per cent
$C_{30}H_{52}O_2$ requires C = 81.01 per cent, H = 11.80 per cent
$C_{30}H_{54}O_2$ requires C = 80.65 per cent, H = 12.19 per cent

Thus the substance contained oxygen.

Although molecular weight determination was omitted, judging from its boiling points, it is very likely that the substance had a molecular weight approaching that of squalene. Of the two chemical formulas, the former agrees more closely with the analytical results (the calculated iodine value of $C_{30}H_{52}O_2$ is 285.6). Then the compound was probably a dihydroxylated derivative of squalene of the formula $C_{30}H_{50}(OH)_2$. Employing the n^2 formula, the specific refraction of the substance is 0.3248, and the molecular refraction 144.3. Adopting Eisenlohr's numbers, the calculated molecular refraction for $C_{30}H_{52}O_2$ with five double bonds is 141.5 (assuming the O as forming the OH group).

On passing dry HCl to the ethereal solution of this substance, squalene hexahydrochloride was regenerated.

FORMOLITE—According to Marcusson,[1] 9 g. of squalene were dissolved in 17 cc. of normal benzene and 10 cc. of concentrated sulfuric acid were added. While well-cooled, 5 cc. of formaldehyde solution were added and well shaken. After 30 minutes' standing, the solution was poured into 70 cc. of water and neutralized with ammonia. A pale yellow precipitate formed and was well washed with benzene and water. The yield was 1.7 g. The dried formolite was pale yellow in color; it turned reddish brown at 150° C. and decomposed at about 180° C. Its elementary analysis gave 67.99 per cent C and 8.79 per cent H. The substance, therefore, contained more than 20 per cent of O. From the filtrate, unchanged squalene was recovered.

NITROSOCHLORIDE—2.5 g. of squalene, 2.5 g. of glacial acetic acid, and 4 g. of amyl nitrite were mixed, and on cooling the vessel with ice and salt, 0.75 cc. of 33 per cent hydrochloric acid was added. No crystalline compound was obtained.[2]

NITROSITE—Solutions of 5 g. of sodium nitrite in 8 g. of water and of 5 cc. of squalene in 10 cc. of petroleum ether were mixed. On cooling the mixture with ice and salt, 5 cc. of acetic acid were added and well shaken. On standing over one night, an orange-yellow resinous substance was formed, but no further examination was made.

DRY DISTILLATION—By repeated distillations of 200 g. of squalene under atmospheric pressure, a fraction (18.5 g.) boiling at 165° to 175° C., with sp. gr. (15°/4° C.) 0.8193, and refractive index (20° C.) 1.4630 was obtained. It was then fractionated under 13 mm. pressure as follows:

Fraction	Temperature of Distillation	Yield Grams	Sp. Gr. (15° C.)	Ref. Ind. (15° C.)
1	Below 60° C.	5	....	1.4605
2	60–65°	4.3	0.8180	1.4621
3	65–69°	4	....	1.4643

Results of elementary analysis of Fraction 2 were as follows:

0.1374 substance gave 0.4392 CO_2, 0.1558 H_2O

$C = 87.18$ per cent, $H = 12.69$ per cent

Molecular weight determined by the freezing-point method using benzene as solvent was 131.

The substance was, therefore, a hydrocarbon.

On comparing it to the aliphatic terpene, myrcene, it was observed that it had a little higher specific gravity and a lower refractive index. The ratio of C to H was 10 : 17.3.

Whether the substance contained myrcene or not was undecided.[1]

OXIDATION OF SQUALENE—Squalene was oxidized with alkaline potassium permanganate solution. As a chief oxidation product, a light brown viscous substance soluble in water and insoluble in ether and petroleum ether was obtained. As no definite compound was isolated, the details are omitted here.

APPROXIMATE QUANTITATIVE DETERMINATION OF SQUALENE

In technical and other applications of squalene it is necessary to determine at least approximately its percentage in a given sample of shark liver oil. As already stated it is often possible to know the rough content of squalene by the fractional extraction of the unsaponifiable matter with petroleum ether; but the result becomes very uncertain when the oil contains some liquid alcohols. The detection of squalene by means of the hexahydrochloride is very delicate, but as it is difficult to change the whole of the hydrocarbon into this compound, the reaction is not applicable for the determination of squalene.

According to the writer's experiments, a simple and comparatively accurate determination of squalene is effected by the distillation of the sample of the oil under a diminished pressure. Although the method is not strictly accurate it is sufficiently exact from the technical point of view, inasmuch as the hydrocarbon may only be isolated from shark liver oil by distillation on an industrial scale.

To perform the determination, a not too large sample of the oil is distilled under at least 10 mm. pressure in the current of an indifferent gas. The operation adopted by the author is as follows:

50 g. (weighed accurately to 0.1 g.) of the oil are placed in a distillation flask[2] of about 150 cc. capacity. The neck of the flask is closed with a cork having two holes; to the one hole, a thermometer is inserted, while the other holds a glass tube, the lower end of which is drawn to a capillary tube and reaches nearly to the bottom of the flask. The upper end of the tube is connected to a Kipp CO_2 generator with a stout rubber tube having a screw pinchcock. The delivery tube of the flask is directly inserted by means of a cork into another distillation flask (previously weighed) of somewhat smaller capacity which serves as the receiver of the distillate. The delivery tube of the receiver flask is attached to a vacuum or water pump. The distillation flask is placed on an oil bath which is gradually heated to a final temperature of about 310° C., while the air is exhausted from the flask, and by the suitable turning of the screw pinchcock carbon dioxide is bubbled into the oil. The pressure is maintained at about 10 mm.

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[1] *Chem. Zentr.*, **1911**, 729.

[2] Chapman, *Loc. cit.*

[1] Recently, B. Kubota (*J. Tokyo Chem. Soc.*, **1918**, 879) obtained isoprene and hydromyrcene $C_{10}H_{18}$ by the dry distillation of squalene. The same chemist has also investigated the chemical constitution of squalene by the decomposition of the ozonide, and concluded that squalene is an animal terpene; see also Chapman, *Loc. cit.*

[2] The Claisen flask is preferable.

TABLE III

SAMPLE	Pressure (Mm.)	Distillation Temperature (° C.)	DISTILLATE				Squalene Approximate Percentage
			Grams	Appearance	Acid Value	Ref. Index (20° C.)	
(1) Ai-zamé oil No. 1	9.0	260–262	42.5	Pale yellow liquid	0.37	1.4955	84.8
Ai-zamé oil No. 2	9.5	262–263	41.3	Pale yellow liquid	0.37	1.4965	82.4
(2) Imori-zamé oil	2.0	235–245	39.8	Nearly colorless liquid	0.51	1.4957	79.4
(3) Heratsuno-zamé oil	9.0	261–263	29.3	Pale yellow liquid	1.03	1.4950	58.3
(4) Frill-shark oil No. 1	2.0	Chiefly 235	3.7	Yellow liquid	8.28	1.4879	7.1
(7) Birodo-zamé oil No. 1	9.0	261–262	14.2	Yellow liquid	5.99	1.4955	27.6
Birodo-zamé oil No. 2	9.0	259–261	9.9	Pale yellow liquid	2.80	1.4953	19.5
(9) Kinbei-zamé oil	2.0	Chiefly 235–237	15.2	Pale yellow liquid	0.94	1.4963	30.3
(10) Kanatsubo-zamé oil	2.0	Chiefly 235–238	15.0	Pale yellow liquid	0.87	1.4947	29.9
(11) Vume-zamé oil	9 0	Chiefly 257	12.3	Pale yellow liquid	2.62	1.4951	24.3
(12) Kuroko-zamé oil	9.0	Chiefly 256	7.0	Pale yellow liquid	7.14	1.4920	13.5
(13) Basking-shark oil No. 1	9.0	254–259	14.2	Yellow liquid with a little solid	16.85	1.4915	26.0

Preliminary experiments were performed with Hokkaidō Abura-zamé oil which did not contain squalene. The following amounts of squalene were added to the oil and the distillation performed. The results were as follows (pressure 9 mm.; final temperature of oil bath, 310° C.):

	Distillate			Squalene
	Gram	Acid Value	Ref. Ind. (20° C.)	Per cent
Ahura-zamé oil 25 g. Squalene 25 g. (= 50 per cent)	24.9	4.3	1.4951	48.8
Abura-zamé oid 45 g. Squalene 5 g. (= 10 per cent)	4.5	17.5	1.4925	8.4

NOTE—The distillate minus free acids was taken as squalene. The free acids were calculated as oleic acid.

It is to be seen from the above results that the error amounted to 1.2 to 1.6 per cent. The results appear to be rather good with this sort of determination.

The results of the determination of squalene in various samples of shark liver oil are shown in Table III.

In the case of samples of unknown origin, more especially when there are some doubts as to adulteration, it is necessary to note the distillation temperature and refractive index of the distillate. The refractive index of the acid-free distillate should be at least above 1.4950 at 20° C.

As Heratsuno-zamé and some basking-shark liver oils contain hydrocarbons besides squalene, the distillates from these oils consist of mixtures of hydrocarbons. In such cases the fractional distillation of the distillate is necessary to obtain squalene in pure state.

If shark liver oil is adulterated with petroleum, the latter mainly boils at lower temperatures than squalene. But with high-boiling petroleum, the separation of the hydrocarbons from squalene becomes very difficult and in some cases probably impossible.

It is interesting to note that the residues obtained by distilling squalene from shark liver oils have nearly equal low refractive indices, as may be seen from the following table:

TABLE IV

RESIDUE FROM	APPEARANCE	Ref. Index (20° C.)
(1) Ai-zamé oil No. 1	Brownish yellow liquid	1.4762
Ai-zamé oil No. 2	Brownish yellow liquid	1.4759
(2) Imori-zamé oil	Brownish yellow liquid	1.4775
(3) Heratsuno-zamé oil	Yellow-orange liquid	1.4700
(4) Frill-shark oil No. 1	Light yellow liquid and cryst. deposit	1.4710
(7) Birodo-zamé oil No. 1	Brownish yellow liquid	1.4770
Birodo-zamé oil No. 2	Light yellow liquid	1.4715
(9) Kinbei-zamé oil	Light yellow liquid	1.4770
(10) Kanatsubo-zamé oil	Orange-yellow liquid and a littl gelatinous ppt.	1.4725
(11) Yume-zamé oil	Light yellow liquid	1.4741
(12) Kuroko-zamé oil	Pale yellow liquid	1.4740
(13) Basking-shark oil No. 1	Brownish yellow liquid	1.4720

The great differences in the refractive indices of the original shark liver oils are therefore chiefly due to the varying amounts of squalene contained in them. The properties of the residual oils appear to resemble each other.

SUMMARY

I—The properties of shark liver oils have been found to differ greatly according to the difference of the species of the fish.

II—Shark liver oils may conveniently be divided into the following two groups:

(*a*) The oils of low specific gravity (below 0.9 at 15°/4° C.).

(*b*) The oils of high specific gravity (above 0.9 at 15°/4° C.).

III—The shark liver oils of low specific gravity invariably contained squalene.

IV—The shark liver oils of high specific gravity, with the exceptions of Higezuno, crow-shark and Fujikujira oils, did not contain squalene.

V—Squalene has been found to occur far more frequently in the liver oils from the sharks belonging to the family *Squalidae*, but the liver oils from Imori-zamé (*Scylliorhinidae*), frill-shark (*Chlamydoselachidae*), Kanatsubo-zamé (*Dalatiidae*) and basking-shark (*Cetorhinidae*) also contained notable amounts of the hydrocarbon.

VI—Some properties of squalene and its derivatives have been described. The formation and isolation of squalene hexahydrochloride, $C_{30}H_{50}.6HCl$, have been confirmed to be the most delicate test for the detection of squalene.

VII—For the approximate quantitative determination of hydrocarbons (especially squalene) in shark liver oils, the distillation of the oil under a diminished pressure has been proposed. 50 g. of the oil are distilled under at least 10 mm. pressure and the acid value of the distillate, calculated as oleic acid, is deducted from the weight of the distillate, the remainder being the approximate quantity of the hydrocarbons.

It may be added here from my latest experiments that squalene occurs only in the oils from certain sharks. No other fatty oils have yet been found which contain this peculiar hydrocarbon.

ACKNOWLEDGMENT

I wish to express my sincere thanks to Mr. Shigeho Tanaka, lecturer in Zoölogy in Tokyo Imperial University, who has kindly examined the fish used for the investigation.

OCCURRENCE OF SQUALENE IN THE EGG OIL FROM SHARK

By Mitsumaru Tsujimoto

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Received May 14, 1919

A female specimen of the shark named Kinbei-zamé, *Lepidorhinus kinbei* (Tanaka), which was used for the examination of liver oil, contained twelve eggs. The eggs were soft and had a light orange-yellow color. They were of large ellipsoidal forms, with longer diameters of about 7 cm., and weighed on an average of 140 g. Nine eggs which had a total weight of 1260 g. were crushed to a paste and heated with an excess of alcoholic potash, then the soap decomposed with hydrochloric acid and the fatty matter taken up with ether. On evaporating off the ether from the extract, 218 g., 17.3 per cent of the fatty matter, were obtained. It was a light brown-colored substance and mainly solidified at the ordinary temperatures. The numerical properties of the substance were as follows:

Specific gravity (15° C.)	0.8997
Acid value	91.3
Saponification value	107.0
Iodine value (Wijs)	177.6
Refractive index (20° C.)	1.4769
Unsaponifiable matter	33.00 per cent

On passing dry HCl into the well-cooled ethereal solution of this substance, about 20 per cent of a white crystalline precipitate was obtained. On recrystallizing it from acetone it sintered at about 110° C. and melted to a clear liquid at 123°–124° C.

0.2470 substance gave 0.3374 AgCl (Carius method)
Cl = 33.77 per cent
$C_{30}H_{50}.6HCl$ requires 33.82 per cent Cl

The substance has therefore been confirmed to be squalene hexahydrochloride.

As the eggs were separated very carefully from the body of the shark, there is no doubt as to the absence of the liver oil in the egg oil. Subsequently squalene has been directly extracted from the dried eggs with ether.

The egg oil from frill-shark, *Chlamydoselachus anguineus* (Garman), has also been found to contain squalene.

LABORATORY AND PLANT

CONSTANT TEMPERATURE STILL HEAD FOR LIGHT OIL FRACTIONATION[1]

By Frederick M. Washburn

Bureau of Standards, Washington, D. C.

Received May 22, 1919

GENERAL CONSIDERATIONS

Because of the greatly increased production of coke-oven light oil, and the growing importance of the benzol industry, it was felt that a more accurate method of analysis for light oils was needed, as there is frequently a great discrepancy between the results of analysis of the same light oil, using different methods, and between the results obtained by different analysts, using the same method. This paper represents the results of a brief search for an improved method for the determination of benzene, toluene, and solvent naphtha in coke-oven or coal-tar light oil.

After the light oil has been passed through the usual treatment for the determination of the percentage of wash oil present and the determination of the percentage of loss on washing with concentrated sulfuric acid, it is practically a mixture of benzene, toluene, the three isomeric xylenes, and higher aromatic hydrocarbons, together with the small amounts of paraffins usually present. The xylenes and the higher hydrocarbons boiling between 135° and 160° C. are classed as solvent naphtha, so that the problem resolves itself into a separation of a mixture of benzene, toluene, and solvent naphtha. Fractional distillation furnishes the easiest means of accomplishing this.

There are three main types of methods generally in use for the fractional distillation of light oil. In the first of these, the light oil is distilled through a fractionating column and separated into two fractions, one a mixture of benzene and toluene, and the other a mixture of toluene and xylene. A portion of each of the two fractions obtained is subjected to distillation in a side-neck flask, and the percentages of benzene and toluene and of toluene and xylene are read off from the curves or tables giving the relation between the composition of the fraction distilled and the temperature of distillation. The method of Hugh W. James[1] is an example of this type. This method is open to objection on account of the serious errors introduced by the estimation of the percentage composition from the boiling-point curves or tables, since small amounts of impurities materially influence the boiling points of the fractions.

In the second type of method, distillation is made through an efficient fractionating column, and the receiver is changed at 95° C. and at 125° C. The fraction under 95° C. is considered as benzene, the fraction 95° to 125° C. as toluene, and the residue as solvent naphtha. The method of Gustav Egloff[2] is an example of this type.

This method is more logical than the first, since it aims at a more complete separation of the mixture, but it gives fractions which are not pure. The first fraction consists of a mixture of benzene and toluene; the second of benzene, toluene, and xylene; and the residue of toluene and xylene. The results obtained depend upon the assumption that there is the same amount of toluene in the benzene fraction as there is benzene in the toluene fraction, and, similarly, as much xylene in the toluene fraction as there is toluene in the residue, in which case the errors introduced by assuming the fractions to be pure would neutralize each other. The objection to this method is that this relation does not usually exist, since the amount of toluene distilling below 95° C., the amount of benzene distilling above 95° C., and the amount of xylene distilling below 125° C. vary with the rate of distillation, efficiency of the column, composition of the oil, etc.

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[1] Published by permission of the Director of the Bureau of Standards.

[1] *J. Soc. Chem. Ind.*, **35** (1916), 236.

[2] *Met. & Chem. Eng.*, **16** (1917), 259.

In the third type of method, the light oil is separated into the largest possible fractions which distill respectively below 81.0° C. (for benzene), and from 109.0° to 111.5° C. (for toluene). The intermediate fractions (81.0° to 109.0° C. and 111.5° to 137.0° C.) are then subjected to distillation in a side-neck flask. The percentage composition of the intermediates is then read off from previously constructed curves, similar to those in Figs. 3 and 4. The amounts of benzene, toluene, and xylene obtained from these intermediates are added to the benzene, toluene, and solvent naphtha fractions, respectively, to give the total percentages. The method of Dyke Wilson and Ivan Roberts[1] is an example of this type. This method is the most logical of the three, since the percentage composition of the intermediates is actually determined, giving less probability of error than if the percentages were taken as some arbitrary amount. Furthermore, the error introduced by estimating the percentage composition by boiling point curves is comparatively small since it is applied to small volumes.

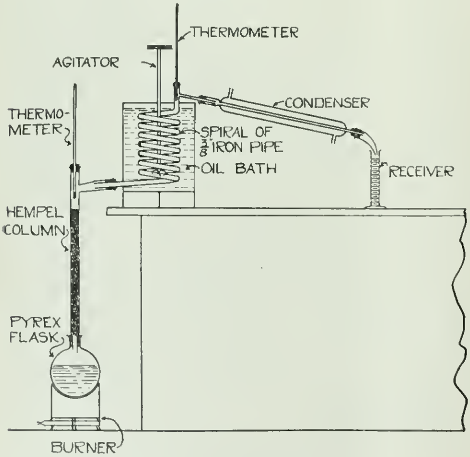

FIG. 1—CONSTANT TEMPERATURE STILL HEAD

The fractionating apparatus used by Wilson and Roberts consists of a 40 in. Hempel column, filled for 36 in. of its length with glass beads; above this is a vertical reflux condenser, the purpose of which is to condense out the higher boiling constituents, and allow only the lower boiling constituents to pass. The objection to this form of apparatus lies in the difficulty of control of the temperature of the reflux condenser, or dephlegmator. This temperature is regulated by the flow of liquid through the jacket of the condenser. Near the end of a fraction the variation of 0.2° C. in the temperature will mean the difference between completely condensing the vapors and allowing the lower boiling constituent to pass. For this reason it is practically impossible to use the dephlegmator efficiently, as the temperature is extremely difficult to control with any degree of accuracy.

CONSTANT TEMPERATURE STILL HEAD APPARATUS

DESCRIPTION—The constant temperature still head is merely an improvement on the dephlegmator used in the Wilson and Roberts still. With its use it is possible to control absolutely the vapor temperature, thus making it possible to condense out practically the last traces of constituents having a higher boiling point than the fraction desired. It is not a new idea, but was first worked out by Frederick A. Brown.[1]

The fractionating apparatus used in the experiments described in this paper, consisted of two parts, a Hempel column and the constant temperature still head. This latter consisted of a spiral of iron pipe immersed in a bath of oil. The temperature of the oil bath was controlled by means of a thermostat, the bath being heated electrically, and stirred by a motor-driven agitator.

The pipe spiral was made from a 12 ft. length of $^3/_8$ in. wrought iron pipe bent cold around a mandrel of 5 in. diameter, giving a coil of about 6 in. diameter and $^3/_4$ in. between the turns. A piece of copper tubing ($^1/_4$ in. inside diameter) was soldered to the coil as shown, to act as the outlet to the condenser.

The Hempel column was made of glass, $1^1/_8$ in. inside diameter, and so formed that a thermometer could be inserted in the top. A metal column would be better, because there is danger from fire in case of breakage of the glass column. A 1500 cc. pyrex glass flask was used, but here again metal would be more suitable, for the same reason. The flask was heated by means of a Rose burner with a hemispherical top covered with an asbestos covered gauze. Three high precision thermometers (70° to 200° C.) were used, one at the top of the Hempel column, one at the top of the spiral, and one immersed in the oil bath (this last not shown in the figure).

OPERATING DIRECTIONS—The bath was brought up to the required temperature by means of a coil of resistance wire immersed in the bath, and was maintained at that temperature by means of four 50-watt tubular carbon lamps. A mercury thermoregulator of the usual type, used with a relay, controlled the temperature of the bath to 0.2° C.

A 1000 cc. sample, measured at 15.5° C., was used. The temperature of the bath was brought rapidly up to 75° C. by means of the heating coil, and then slowly up to the temperature necessary to allow the vapors to pass through the coil when the liquid in the flask was boiling briskly. The temperature of the oil bath was then controlled by regulation of the thermostat so that 3 to 4 drops per sec. fell from the end of the condenser. This temperature was about 0.1° C. below the vapor temperature at the top of the still head, as may be seen from the curve given in Fig. 2. Toward the end of the benzene fraction it was necessary to raise the temperature of the bath to allow the vapors

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[1] *Gas Record*, March 1916, p. 210.

[1] *Trans. Chem. Soc.*, **37** (1880), 49.

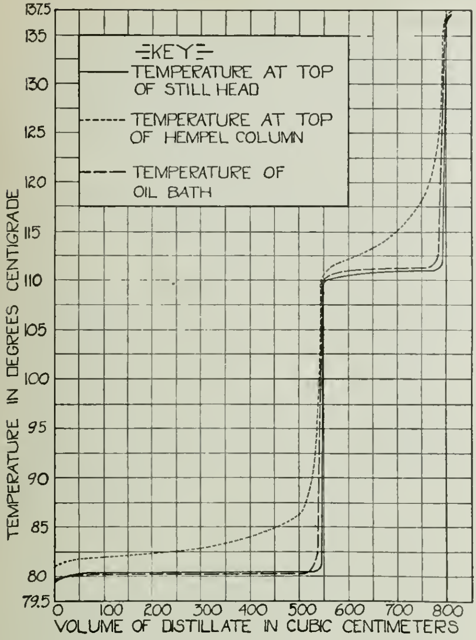

Fig. 2—Typical Distillation Curves Obtained with the Constant Temperature Still Head

to pass through. This was done gradually, keeping the vapor temperature at the top of the still head under 81° C. The rate of distillation gradually slowed down to about 1 drop per 10 sec., when the temperature of 81° C. was reached. The receiver was then changed and the temperature of the bath gradually raised, keeping the rate of distillation under 1 drop per sec. until a temperature of 110.0° C. was reached. The receiver was then changed, and the temperature of the oil bath was held by the thermoregulator to such a temperature that the rate of distillation was about 2 drops per sec., and the vapor temperature was under 111.5° C. Near the end of the toluene fraction it was necessary to raise the temperature of the bath, as was done in the benzene fraction, until the temperature of 111.5° C. was reached. The receiver was then changed and the temperature of the oil bath gradually raised, keeping a rate of distillation of under 1 drop per sec., until the temperature of 137.0 C. was reached. The distillation was then stopped and the residue allowed to cool. Then the residue was drained carefully into a graduate and measured.

The intermediate fractions were distilled in a standard boiling-point apparatus,[1] except that a 50 cc. pyrex flask was used in place of the larger flask, and the rate of distillation kept at 1 drop per sec. A 60° to 140° C. thermometer, graduated in 0.2°, was used. The temperature at which exactly one-half of the liquid passed over was noted, and the percentage of benzene and toluene, and of toluene and xylene read off from previously constructed curves (Figs. 3 and 4). The amounts of benzene and toluene obtained from the intermediate fractions were added to the amounts obtained in the benzene and toluene fractions to give the percentage of benzene and toluene, and the amount of xylene obtained from the toluene-xylene intermediate fraction added to the residue to give the percentage of solvent naphtha. The distillation loss was determined by subtracting the total amount of distillate plus the residue from the volume taken for distillation. All volume measurements were made at a temperature of 15.5° C.

RESULTS OBTAINED—Table I gives the results of fractionating mixtures made up of known amounts of pure benzene, toluene, and xylene, and shows the high degree of accuracy obtainable. It also shows that the apparatus works equally well with varied percentages of benzene, toluene, and xylene, even though one of the components may be present in a comparatively small amount.

Table I—Results of Distillation of Mixtures of Known Composition

Distillation No.	Benzene Present Per cent	Benzene Found Per cent	Toluene Present Per cent	Toluene Found Per cent	Xylene Present Per cent	Xylene Found Per cent	Distillation Loss Per cent
I	80.00	80.05	10.00	9.99	10.00	9.93	0.03
II	70.00	70.12	20.00	19.81	10.00	9.84	0.23
III	67.50	67.52	17.50	17.22	15.00	14.80	0.46
IV	57.50	57.59	30.00	29.87	12.50	12.47	0.05
V	55.00	55.07	25.00	24.72	20.00	19.85	0.36
VI	40.00	40.18	45.00	45.02	15.00	14.69	0.11
VII	30.00	29.92	55.00	55.66	15.00	14.40	0.02
VIII	20.00	20.21	67.50	67.65	12.50	12.04	0.10
IX	10.00	10.47	75.00	75.16	15.00	14.09	0.28

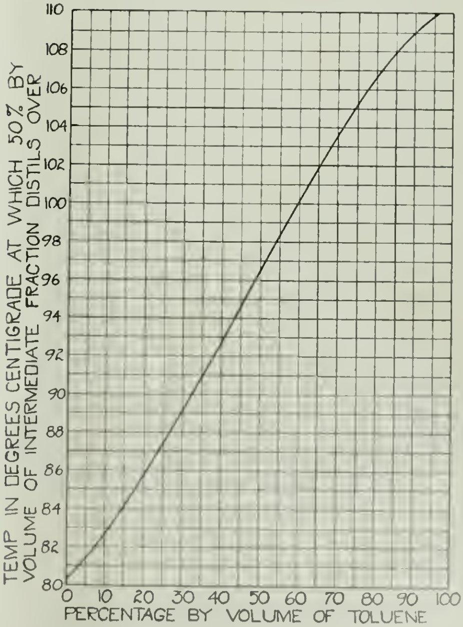

Fig. 3—Benzene-Toluene Intermediate

Fig. 2 shows a set of typical distillation curves obtained with the apparatus. The line showing the temperatures at the top of the Hempel column gives an idea of how the distillation would proceed if only a Hempel column of this length were used. The line showing the temperature at the top of the constant temperature still head shows how the still head condenses out the higher boiling constituents, allowing only the lower boiling ones to pass, thus holding the temperature well within the range allowed for "pure" fractions. As may be seen from the curve, when the temperature at the top of the still head rises to 81.0° C., the upper limit for the benzene fraction, the temperature at the top of the Hempel column is about 105° C., showing that the vapor at that point consists almost entirely of toluene, with only a small amount of benzene, so that practically the only benzene remaining is in the form of vapor in the coil of the still head. Theoretically, it is possible to allow all of the benzene to pass through the coil and into the receiver without allowing any of the toluene to pass, but practically, this would be very difficult and tedious, if not impossible, so that it is much easier to "sweep out" these last small amounts of benzene with toluene, thus giving a small intermediate fraction.

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[1] This Journal, 10 (1918), 1006.

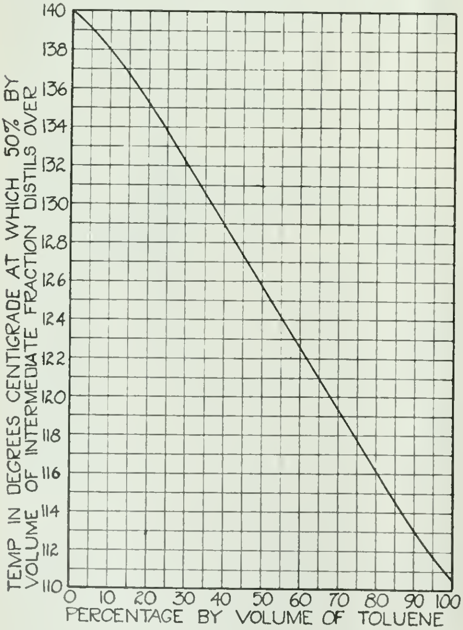

Fig. 4—Toluene-Xylene Intermediate

The same considerations apply to the latter part of the toluene fraction and to the toluene-xylene intermediate.

The large volumes of "pure fractions" and likewise the degree of their purity is shown by the length and straightness of the curve within the temperature ranges of 80° to 81.0° C. and 110.0° to 111.5° C., and the sharpness of separation by the very small rounding of the curves at the points where the receivers are changed (81.0° C., 110.0° C., and 111.5° C.).

The comparatively high degree of purity of the fractions obtained with this apparatus is shown by Table II, which also shows the method of calculation used.

Table II—Results of a Typical Distillation with the Constant Temperature Still Head

Mixture distilled contained 57.50 per cent benzene, 30.00 per cent toluene, and 12.5 per cent xylene. All temperatures are corrected.

BENZENE FRACTION (under 81.0° C.) = 565.8 cc.

Specific gravity at $\frac{15.5° \text{ C.}}{15.5° \text{ C.}}$ = 0.884.

Distillation of Fraction in Standard Boiling Point Apparatus

	Deg. C.
1st drop	80.0
5 cc	80.1
50 cc	80.3
95 cc	81.3
Dry	82.5
Range	2.5

BENZENE-TOLUENE INTERMEDIATE (81.0° to 110.0° C.) = 12.1 cc., one-half distilled over at 85° C.

From curves
83 per cent benzene = 10.11 cc. (to be added to benzene fraction)
17 per cent toluene = 2.0 cc. (to be added to toluene fraction)

TOLUENE FRACTION (110.0° to 111.5° C.) = 289.2 cc.

Specific gravity at $\frac{15.5° \text{ C.}}{15.5° \text{ C.}}$ = 0.870.

Distillation of Fraction in Standard Boiling Point Apparatus

	Deg. C.
1st drop	110.0
5 cc	110.2
50 cc	110.5
95 cc	112.8
Dry	113.2
Range	3.2

TOLUENE-XYLENE INTERMEDIATE (111.5° to 137.0° C.) = 15.0 cc., one-half distilled over at 125° C.

From curves
52 per cent toluene = 7.8 cc. (to be added to toluene fraction)
48 per cent xylene = 7.2 cc. (to be added to xylene fraction)

RESIDUE (above 137.0° C.) = 117.5 cc.

Final Results

Fraction	Volume Found Cc.	Percent Found	Percent Actually Present	Error Per cent
Benzene	575.9	57.59	57.50	+0.09
Toluene	298.9	29.89	30.00	—0.11
Xylene	124.7	12.47	12.50	—0.03
Loss	0.5	0.05	...	..

SUMMARY

The three types of methods generally in use for the fractionation of light oil and the determination of benzene, toluene, and solvent naphtha, are discussed. An apparatus which is an improvement on the dephlegmator of the Wilson and Roberts still is described, and the details of its operation are given. The apparatus is easily and inexpensively constructed, and requires no greater attention or time than others used. Exceptionally large volumes of "pure" fractions are obtained which have a very small boiling-point range, showing that they contain only negligible amounts of impurities. Almost all of each of the components of the mixture distilled is obtained in practically the pure state since the volumes of each of the intermediate fractions are only about 1.5 per

cent of the volume taken for distillation. The composition of each of the intermediate fractions is actually determined, and the error introduced by this determination is small, since it is applied to only small volumes. The apparatus works well on mixtures containing widely varying percentages of benzene, toluene, and solvent naphtha.

FUEL VALUE OF VOLATILE LIQUID MIXTURES

By George Barsky
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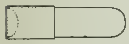
Received August 14, 1919

The gasoline substitutes now coming on the market are, in general, mixtures of very volatile with less volatile liquids. When a bomb calorimeter is employed in the usual way to determine the fuel value of such a mixture, difficulties are encountered. It is extremely difficult to weigh out a sample owing to its volatility and it is next to impossible to get complete combustion.

Attempts to burn in the open pan, in glass bulbs, mixed with other materials, and other common modifications did not give satisfactory results with a fuel containing constituents of volatility varying from ether to kerosene.



The difficulties were finally surmounted in a simple way by the use of gelatin capsules of a particular shape. These were constructed of ordinary capsules by turning in the caps so that they fitted the menisci when the capsules were filled. In this way all the air was excluded. The igniting wire was wound several times around the capsule, which was allowed to rest in the pan. This modification was very successful, giving results that checked within 60 B. t. u., *i. e.*, as close as was obtained on solid fuels with the same calorimeter.

THE McCRUDDEN GRAVIMETRIC CALCIUM METHOD MODIFIED

By J. O. Halverson and J. A. Schulz
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Received July 22, 1919

The results obtained by the substitution of the volumetric asbestos Gooch method for the gravimetric procedure in the McCrudden calcium method have facilitated the determination of the small amounts of calcium which have to be determined in biological and agricultural products. It is thought these results are of sufficient interest to warrant their publication.

McCrudden[1] was unable to employ the Gooch crucible on hardened filter point and suction to advantage in filtering calcium oxalate. He says:

> When Gooch crucibles were tried, it was found that thin layers of asbestos did not retain the precipitate. When layers thick enough to retain the precipitate were used, they soon clogged up and prevented passage of the fluid.

The use of *ignited* non-reducing asbestos in filtering calcium oxalate would greatly facilitate the estimation of small amounts of calcium by the potassium permanganate method rather than by the gravimetric procedure. Therefore if the precipitate and asbestos in the Gooch crucible could be washed into an Erlenmeyer flask it could be heated and titrated at once with a considerable saving of time.

It is apparent from the number of modifications[1] proposed from time to time for the estimation of calcium in feeds and agricultural products that this estimation is not readily done without contamination.[2] An occasional contamination with iron occurs in two substances, wheat bran and raw rock phosphate. The proposed modification may also be used as a means of eliminating this troublesome iron, which is occasionally occluded by the calcium oxalate precipitate in the gravimetric procedure, discoloring somewhat the calcium oxide, causing slightly higher results (0.008 per cent). The McCrudden method[3] has given good results on both biological and agricultural products for the past two and one-half years and the present modification has been in use during the past year.

PREPARATION OF THE ASBESTOS—High grade *ignited* long-fibered asbestos was used. The ignited asbestos was placed in hot sulfuric acid (1 : 5) and digested one hour at 60° to 70° C., with occasional shaking while adding a few drops of $KMnO_4$, keeping at a faint purple tint, and the beaker was kept covered. The material was then placed on a Büchner funnel and washed with distilled water containing a faint tint of $KMnO_4$ until free of acid. This is preserved for future use free from dust and dirt.

PREPARATION OF THE GOOCH CRUCIBLE—The Gooch crucibles of moderate thickness which filter readily at two to three atmospheres pressure, are prepared with some care, using the treated ignited asbestos of three grades of fineness. The separation into three grades of fineness—very fine, medium, and coarse—is done by shaking, decanting, and separating the asbestos in water into three Erlenmeyer flasks. The long, coarse fibers are first used for a foundation, next the medium fibers to fill the interstices, and finally for a compact top layer, the fine sediment which settles slowly in water. Properly prepared Gooch crucibles[4] have given no trouble in filtering precipitates of calcium oxalate.

TITRATION OF THE CALCIUM OXALATE—After the calcium oxalate precipitate is washed free from oxalate and oxalic acid, the precipitate and pad are transferred with a small quantity of hot water to an Erlenmeyer flask and titrated immediately at 65° C., using sulfuric acid (1 : 5).

It is well known that the volumetric method is apt to run slightly lower when the calcium oxalate precipitate is washed off the filter paper with hot water, the usual procedure before titration. This extent is shown

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[1] *J. Biol. Chem.*, **10** (1911), 194.

[1] S. B. Kuzirian, *J. Am. Chem. Soc.*, **38** (1916), 1996.

[2] In plant analysis Mn is apt to be occluded. The revised official method recommends that calcium be reprecipitated. Report of Committee on Editing Tentative and Official Methods of Analysis of the A. O. A. C., **1916**, 31.

[3] *J. Biol. Chem.*, **7** (1910), 83; **10** (1911), 87.

[4] Ignited asbestos improves with use. After each set of filtrations it is freed from acid and saved for further use

TABLE I—EXTENT OF LOSS IN VOLUMETRIC METHOD, USING FILTER PAPER; AMOUNT OF IRON OCCLUDED BY GRAVIMETRIC METHOD

SAMPLE	Detn. No.	Charge, Gram	Grav. CaO, Gram	Grav. Ca, Gram	VOLUMETRIC Calcium Gram	VOLUMETRIC Calcium Per cent	Iron Oxide Occluded, Gram	Grav. Ca, Per cent.	Diff. between G. and V. Method, Per cent.
Bone Ash 1454	1	0.25	0.1348	0.09634	0.0962	38.484	....	38.534	0.050
	2	0.25	0.1352	0.09662	0.0961	38.440	....	38.684	0.244
	3	0.25	0.1346	0.09619	0.0959	38.340	....	38.477	0.137
	4	0.25	....	.....	0.0961	38.440	....	....	...
	AVERAGE					38.426		38.565	0.139
Wheat Bran 1440	5	20.0	0.0282[1]	0.0202	0.0189[2]	0.095	0.0012	0.101	0.006
	6	20.0	0.0306	0.0219	0.0189	0.096	0.0029	0.109	0.014
	7	20.0	0.0276	0.0197	0.0192	0.096	0.0006	0.009	0.003
	AVERAGE					0.095		0.103	0.008

[1] The precipitates had an iron oxide color.
[2] The Gooch filter, not filter paper, was used in this reprecipitation.

TABLE II—RESULTS BY THE VOLUMETRIC ASBESTOS GOOCH METHOD WITH USUAL CHARGE AND WITH SMALL CHARGE (1/5)

SAMPLE	Det. No.	Charge Gram	VOLUMETRIC Calcium Gram	VOLUMETRIC Calcium Per cent	Grav. Calc. Per cent
Bone Ash 1454	7	0.0750	0.02897	38.627	....
	8	0.0750	0.02908	38.779	....
	9	0.0750	0.02908	38.779	....
	10	0.0750	0.02897	38.627	....
	AVERAGE			38.688	38.565
	11	0.3500	0.13512	38.612	
	12	0.3500	0.13512	38.612	
	13	0.3500	0.13527	38.649	
	14	0.3500	0.13504	38.584	
	15	0.3500	0.13516	38.616	
	AVERAGE			38.616	

SUMMARY

METHOD	Calcium Per cent	Diff. bet. Vol. and Grav. Methods
Gravimetric	38.553	......
Volumetric with Filter Paper	38.426	—0.14
Volumetric with Gooch Filter small charge	38.688	+0.12
Volumetric with Gooch Filter, usual charge	38.616	+0.05

by representative results in Table I. The lower result obtained by the use of filter paper is probably due to the loss of a small quantity of the precipitate enmeshed in its fibers. Placing the filter paper in the hot sulfuric acid when almost at the end-point in titration is not feasible when the quantity of calcium oxalate is small. This interferes with the definiteness of the end-point. Therefore it is proposed to use non-reducing ignited asbestos in place of the filter paper in a Gooch crucible, as shown in Table II. The results then closely check the gravimetric procedure, the difference being 0.05 per cent higher, or an error of 0.13 per cent. For small quantities of calcium oxalate the difference is slightly greater, as shown in Table II.

The volumetric results on bone ash (Table I) are one- to two-tenths of a per cent lower than the gravimetric, or a difference of one-third of a per cent. This percentage in samples containing less calcium would of course be greater. In the gravimetric method approximately one-tenth gram of CaO was weighed.

The gravimetric CaO precipitate containing iron oxide, from the wheat bran sample, was dissolved in acid, filtered, and the calcium reprecipitated and determined volumetrically, using the asbestos Gooch pad for filtering off the calcium oxalate which was transferred with the pad to the sulfuric acid and titrated with potassium permanganate with the following results: an average of 0.0021 g. iron oxide was present in the CaO precipitate. This gave a high result, amounting to 8.2 per cent.

Table III gives results on urine and feces, compared with gravimetric results on the same samples. The volumetric results are taken from our daily records. The results on feces of both methods agree within an average of 0.026 per cent. For urine, the modified method checks the gravimetric within an average of 0.25 mg. calcium per 100 cc.

TABLE III—RESULTS BY THE MODIFIED MCCRUDDEN METHOD COMPARED WITH THE GRAVIMETRIC PROCEDURE

SAMPLE	Det. No.	Charge Grams	GRAVIMETRIC CaO Gram	GRAVIMETRIC Calcium Gram	GRAVIMETRIC Calcium Per cent	Det. No.	Charge Grams	VOLUMETRIC Calcium Gram	VOLUMETRIC Calcium Per cent	Difference Per cent
Swine Feces[1] 1530	16	4.9474	0.0302	0.0216	0.436	19	4.4124	0.0178	0.403	0.033
	17	5.0150	0.0310	0.0222	0.442	20	4.6182	0.0185	0.400	0.042
	18	4.8630	0.0300	0.0214	0.441	21	4.3290	0.0177	0.408	0.033
	AVERAGE				0.440		AVERAGE		0.404	0.036
1532	22	4.6357	0.0198	0.0142	0.305	25	5.2118	0.0152	0.291	0.014
	23	3.9106	0.0168	0.0120	0.307	26	4.9386	0.0145	0.293	0.014
	24	3.5862	0.0156	0.0112	0.311	27	4.2078	0.0124	0.295	0.016
	AVERAGE				0.308		AVERAGE		0.293	0.015
Swine Urine[2]		*Cc.*			*G per 100 cc.*		*Cc.*		*G. per 100 cc.*	*G. per 100 cc.*
1549	28	200	0.0176	0.0126	0.0063	31	200	0.0118	0.0059	0.0004
	29	200	0.0176	0.0126	0.0063	32	200	0.0119	0.0060	0.0003
	30	200	0.0172	0.0123	0.0062	33	200	0.0119	0.0060	0.0002
	AVERAGE				0.0063		AVERAGE		0.0060	0.0003
1552	34	200	0.0092	0.0066	0.0033	37	200	0.0062	0.0031	0.0002
	35	200	0.0094	0.0067	0.0034	38	200	0.0062	0.0031	0.0003
	36	200	0.0092	0.0066	0.0033	39	200	0.0059	0.0030	0.0003
	AVERAGE				0.0033		AVERAGE		0.0031	0.0002

[1] Feces ashed in both methods. [2] Aqua regia digestion used in both methods, followed by ashing.

CONCLUSION

The volumetric method of estimating calcium in the McCrudden method, substituting the treated ignited asbestos Gooch for filter paper, gives almost identical results with the gravimetric procedure. The method is rapid and the treated ignited asbestos does not tend to reduce $KMnO_4$ in the presence of H_2SO_4 (1 : 5) at 65° C.

The authors wish to thank Dr. E. B. Forbes who made this work possible.

THE EVALUATION OF ALUMINUM DROSS

By F. K. Bezzenberger

LYNITE LABORATORIES, THE ALUMINUM CASTINGS COMPANY, CLEVELAND, OHIO

Received June 30, 1919

The necessity for the recovery of metal from the relatively large quantities of skimmings and dross which occur in the fabrication of aluminum and its alloys has led to the following method for the evaluation of this waste material.

Besides the metals with which aluminum may be alloyed, such as copper, zinc, and iron, this dross contains a high percentage of aluminum oxide, formed by the ready oxidation of the molten metal, and also to a large extent by weathering, the degree of the latter varying with the size of particles and the conditions to which they are subjected.

The solubility of this finely divided oxide in all solvents commonly used for the preparation of alloys for analysis necessitated finding some reagent which will enable the quantitative separation of the metal from it, preferably by taking the latter into solution to facilitate its final determination.

For the purpose of testing various reagents which seemed promising, pure aluminum oxide made by the ignition of the washed hydroxide was used. This material was found to be insoluble to a detectable degree in boiling water, but soluble to a prohibitive degree in acids and alkalies of a strength suitable for the solution of the metal.

The well-known activity of the free halogens with aluminum led to the trial of a saturated water solution of bromine for the purpose, which proved satisfactory, inasmuch as it attacks metallic aluminum vigorously, but does not dissolve the oxide to a detectable degree. This insolubility of the oxide in bromine water, contrasted with its solubility in dilute acids, is explained by the low degree of hydrolysis of bromine in saturated solution, the constant at 25° being 2.4×10^{-8},[1] which is equivalent to 0.013 per cent hydrobromic acid.

On the basis of these qualitative results, a procedure for analyzing aluminum waste was outlined, as follows:

1—Weigh out a representative (0.8 to 1.3 g.) sample of the mixture to be analyzed.

2—Treat with saturated water solution of bromine and add a few drops of free bromine as long as the reaction continues, which depends upon the amount and nature of the sample.

3—If the red color of bromine remains after stirring, the reaction is complete. Drive off free Br_2, digest on a hot plate until color changes to brown, filter, and wash.

4—Precipitate with NH_4OH, wash by decantation three times, filter, and wash with 1 per cent NH_4OH.

Ignite and weigh as usual in this determination.[1]

This gives total aluminum, iron, and adsorbed impurity of copper as oxides. The latter was found in some cases to be as high as 2 per cent. To correct for this, proceed as follows:

1—Treat the oxides in the crucible in a beaker with sulfuric acid, 5 to 10 cc. acid to 100 cc. solution. This dissolves Fe_2O_3, CuO, and some Al_2O_3.

2—Electrolie for copper.

3—Reduce the iron by passing the solution through a Jones reductor and titrate with permanganate.

4—Calculate CuO and Fe as Fe_2O_3, and subtract from the total oxides.

5—This gives Al_2O_3. Calculate as aluminum.

Following this procedure, a number of synthetic samples consisting of metallic aluminum and aluminum oxide in amount from zero to 45 per cent of the sample, were analyzed. The results are given in the following table:

Wt. of Sample	Per cent Al_2O_3	Al_2O in Sample	Aluminum in Sample	Aluminum Found	Error Based on Aluminum Per cent
0.6160	0	0	0.6160	0.6177	+0.27
0.5642	0	0	0.5642	0.5633	—0.16
0.4104	5	0.0231	0.3873	0.3880	+0.18
0.3063	7	0.0230	0.2833	0.2830	—0.11
0.5791	18	0.1038	0.4753	0.4768	+0.32
0.3538	30	0.1013	0.2525	0.2517	—0.32
0.4098	45	0.1847	0.2251	0.2257	+0.29

The results indicate that the method is entirely satisfactory for the purpose and it has been adopted and used in our laboratories.

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[1] Bray, *J. Am. Chem. Soc.*, **32** (1910), 932.

[1] Bureau of Standards, *Bulletin* **286**.

ADDRESSES AND CONTRIBUTED ARTICLES

THE VALUE OF COST ACCOUNTING IN COMMERCIAL LABORATORIES[1]

By William W. Caswell

Treasurer, Arthur D. Little, Inc., Cambridge, Mass.

I truly appreciate the honor of being invited to present this paper before you to-day, and it is with diffidence that I approach the subject of cost accounting as applied to chemical laboratories, but I have found the knowledge of costs of the greatest value in every line of business with which I have been connected, and not by any means the least in a commercial laboratory.

Not so very long ago cost accounting was practically unknown, and in the business where it was not employed it was considered a frill and just so much red tape; in fact it was looked upon by the executive of the average corporation as one of the black arts, and most executives had as much knowledge of cost accounting as they had of quadratic equations. The men of sound business principles, however, and those forced by competition or through the nature of their business to make only a small margin of profit on a large output, soon realized the danger of treading an unknown way without a light to guide them. The haphazard methods of guess-work as to what is manufacturing cost may be all very well for a concern making only one article and that of the simplest variety, but take, for instance, the manufacture of automobiles with all the different parts both made and purchased, and the man who attempted to run such a business without an adequate knowledge of the costs would commit financial suicide.

We all look upon the government supervision of our incomes, both individual and corporate, as a necessary evil, but in reality it has not been an unmitigated evil, for this supervision which has been brought about by control of prices and the collection of taxes has taught a great many of us not only the value of keeping accurate accounts, but also the necessity of knowing exactly what our costs are in order to arrive with some degree of definiteness at our profits. Government statistics show that out of over 250,000 corporations in the United States less than half are making money and that only about 5 per cent have any accurate idea of what their costs are. This is a sad showing, and I venture to say that in the case of the 125,000 which are not making money the fault, in a great majority of cases, lies in their not knowing their costs.

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[1] Presented before the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 4, 1919.

Let me point out a few of the advantages of a cost system as applied to general business before taking up the advantages to the commercial laboratory.

In the first place, and I cannot lay too much stress on this point, it makes for greater efficiency in that it enables the heads of the departments to keep in intimate touch with the minute details of their departments, and also enables the executives of a corporation to tell at a glance whether the departments themselves are functioning properly.

In the second place, if certain lines of work are not profitable the cost figures show the reason for the loss. It may be that the cost of manufacture is too great and can be reduced, or it may be that there is excessive waste in time or material; whatever the trouble is, it can readily be ascertained.

In the third place, cost accounting provides a periodical balance sheet which affords a comparison of the business in the different periods, and also shows whether the business as a whole is making steady progress.

And in the fourth place, a cost system necessitates a standardization of the activities of a business with standard methods of obtaining the required data, and makes this data easily available for all sorts of uses.

These few instances I think point out, or at least hint at, in a general way, some of the advantages of knowing the costs. I venture to say that those of you who are not using a cost system to-day would be only too glad of an opportunity to obtain a more intimate knowledge of your business if you had the chance. The advantages of a cost system are well known, not only to all accountants, but to all those executives who have studied accountancy, not with a view of compiling columns of figures, but of accurately reading and understanding what these figures show, and what they mean when applied to the business as a whole.

So much for the general aspect of cost accounting. The question now arises as to how, even if we wish, we can apply this practice to a laboratory, for it can be justly said that you are talking about manufactures and we do not manufacture anything. We have no raw materials which enter into our business; we have no machines on which to figure a machine hour rate; in fact we have no elements in our business to which cost accounting is applicable, but you have, and the fundamentals of cost accounting apply equally as well to the chemist as to the manufacturer. Of course no one system of cost accounting can be laid down to cover all business activities. It is not possible to apply a certain system bodily to any one business group, nor is it possible to take a system and apply it to more than one laboratory without some changes which are essential to the individual business, but the general principles apply to all.

The basic elements of cost are three in number: prime cost, direct expense, and indirect expense. I have found it a great help in any cost system to keep these three great divisions clearly in mind. They of course can be subdivided in various ways, but we should never lose sight of the main divisions. The prime cost is made up of raw materials and direct labor only. Now in a commercial laboratory we have no raw material to deal with; therefore, let us eliminate it from the cost system, which leaves for the prime cost only direct labor; chemicals and apparatus form the direct expense, and overhead or burden the indirect expense. Now certainly with these three elements of prime cost, direct expense and indirect expense, we have something upon which to work, and we can build from this firm foundation a cost system which can be applied directly to any individual laboratory, no matter how large nor how small.

In a commercial laboratory where the work is being done for outside clients, what you are really seeking is the cost of your services, that is, the cost of the salaries of the chemists who are working in the laboratory. Thus the prime cost, or the man's time, plus the direct expense of chemicals and apparatus is the direct cost of the work. To this direct cost must be added indirect expense, such as rent, depreciation, taxes, insurance, light, heat, etc., and also the indirect cost of management and supervision, which may be classed as overhead, in order to arrive at the total cost. Once the total cost of the work is ascertained, the next step is the percentage of profit which is reasonable for the work done, and the final figure is the charge to the client, or selling price.

This latter point, namely, the making of prices, is a very important one. We all have a certain scale of prices at which we take work, but whether we are making a profit on these prices, only a laboratory with a cost system can tell. Some may be too low and our profit as a whole comes from other work; for instance, if we are doing coal and B. t. u. analyses for $5 and water for $35, we may find that we are charging too little for coal and too much for the water analyses, and that a charge of from $10 to $12 on coal is necessary for us to make a reasonable profit and that we can make the same percentage on the water at $25. Besides, with a cost system we then have an actual foundation for our prices and are not merely "following the crowd." A well-rounded price list which provides a recognized margin of profit on all work is bound, in the long run, to make more profit for the concern than large profits on some classes of work, to make up for losses on others taken at too low a figure.

Let us outline for a moment the work of a large laboratory, such as Arthur D. Little, Inc., with which I am familiar. We have coal, water, steel, oils, ores, paints, metals, cements, in fact everything, coming in for analysis. There are manufacturers who are having trouble with their processes as installed and who want them straightened out. There are concerns which want an entirely new process for making some article; individuals who wish to have us construct paper mills, distillation plants, or to change their present plants over to other lines of business. In fact, research problems of the largest magnitude are often put to us on the one hand, while on the other we have those requiring merely the common sense treatment which can be easily handled by correspondence. You can readily see what would happen if the prices for such divergent lines of investigation were to be fixed by guess-work and how important it is in a laboratory of this size to have an accurate idea of the cost of the work upon which one can readily and easily base one's prices.

So these diversified lines lead to a natural division of the work into departments. There is the analytical department, to which all analytical work is assigned, the engineering department for designing and construction work, the research department for research problems, a paper and pulp department, textile department, food laboratory, cement laboratory, and other divisions, if the volume of business warrants. Once a division in the work has been made, the inquiry naturally arises, is such and such a department paying a profit, and to find out you must know accurately the cost of such a department. The same necessity for knowing costs applies to the small laboratory, for the main divisions of a large laboratory can be subdivided to a size comparable with the smallest.

At this point I wish to warn you of the great danger of too elaborate a cost system. The tail may very easily wag the dog, and a system be installed which requires too many clerks to keep it up and which furnishes a lot of useless figures.

Beware of red tape! No system of ascertaining costs should be left to an accountant alone to install. The executive is the person who knows what figures are of value to him and it is the men in charge of the organization who should tell the accountant what they wish to learn from the costs. Start with the very simplest system of collecting costs; it can always be elaborated upon, but the elaborate system if installed at the start will in all probability break down of its own weight and cause discouragement and fault finding.

The great benefit of cost accounting to the executive is derived from the knowledge of how to make use of the figures when once they are collected, and to learn the lesson which they teach. Of course it takes some time to collect the necessary data in a laboratory, to be able to say with certainty that this determination or that requires so many hours, but if over a period of a year we have let us say, one thousand coal analyses and these analyses have been made by three or four men, your figures at the end of the year will give you a pretty good working average for the length of time necessary to make one analysis, and knowing this, one can very easily estimate the average cost of such work and can set the price accordingly. Having arrived at the average time for such analyses, if there comes any wide variation in the cost it immediately attracts attention and the cause for such deviation is at once looked into and corrected.

Leaving the executive and the importance of cost accounting to him for a moment, let us look at the individual chemist who is working at the bench to see of what benefit a cost system is to him.

That cost accounting makes for efficiency there can be no doubt. The individual takes a pride in the quick accomplishment of his work, or if he does not take a pride in it, he knows that his short-comings will be called to the attention of the head of his department.

I have been cautioned not to go into the details of cost accounting in this paper and therefore will not take up the method of collecting the necessary data and applying it to a particular job. Suffice it to say that each chemist in a laboratory works regularly a certain number of hours, and our unit then is the salary cost per hour of each man plus the direct expenses, plus a figure which represents his proportion of the indirect expenses for that hour. Each man turns in a time slip every day showing the number of hours he spent on a case and from this slip the cost figures are made up.

One might imagine from this that the individual chemist has no further interest in the cost system, and that once he has made out his time slips, provided they are only average ones, he can get by and hears nothing more from it. If it took a certain man a short time to make an analysis he gets no praise; if it took him a longer time he is blamed. If cost accounting or a cost system only goes as far as this, it has failed miserably in one of its chief functions. The time spent by each man every day is of course recorded and the time and cost for each case is made out, giving the heads of the laboratories the costs they require, but here comes the application of cost accounting to the individual. As it is necessary to record his time against the case on which he is working, a record of the entire time of the individual is kept, irrespective of what case he may be working on. At the end of the accounting period this individual record shows whether a man has done efficient work or not, and in each case of good work, that man is not only rewarded by praise from the head of his department, but also, in many instances, by a cash bonus, both of which tend to show the individual that his work is appreciated.

I may be pardoned if I go into the details of the cost system for just a moment to bring out this fundamental application of cost accounting to the man at the bench more clearly, and give an example of what I mean. Suppose a man is getting a salary of $1 an hour, or $8 a day, and the proportion of the overhead of that department is another dollar an hour for each man working in it. It would therefore cost the company $2 an hour for every hour of that man's time. Let us also suppose that a certain analysis takes on an average four hours (the length of time having been ascertained from figures compiled over a year or more, and hundreds of similar analyses). We know, therefore, that it will cost $8 to make such an analysis and have determined upon a profit of 25 per cent of the cost as our selling price. This will make the charge to the client for this analysis $10. Now each man's individual record is kept as a profit and loss in dollars and cents on his sheet for each and every case he works on, and his value to the company is shown by the totals of these profit and loss columns at the close of each period. Therefore, if a man completes the analysis mentioned above in the average time of four hours, his individual record will show a profit of $2 on that case. Should he, however, take five hours to do the work which an average man can do in four, his record shows no profit. If, on the other hand, he can complete the analysis in three hours, his profit will be $4. If good work such as this last instance continues, and this man at the bench is earning more for the company by his skill and efficiency than the average, he certainly is entitled to a raise in salary or a cash bonus, besides recognition from his head of the department. In this way you can plainly see the details of cost accounting immediately become of vital interest to the man at the bench and, as I said before, not only lead to pride in his work but to increased efficiency.

To return to the executive,—be sure to draw a distinction between mere details and the information you are trying to acquire. The figures, the totals, and the costs themselves are only incidentals; it is what these figures and costs show that is important. That is, it is the summarized costs which point the trend of the business and it is necessary to have these in order that the information may be available. One can dig into them as deeply as one wishes if one wants to get at the details. A properly organized cost accounting system is a well of information from which can be drawn the conclusions necessary for controlling the entire policies of the business. An executive without a cost system is like a ship without a rudder. He may strike the right course, but the chances are very much against him, and if his competitor has a system of costs he can steer by compass and can forecast with certainty where he will arrive.

If, in this brief paper, I have succeeded in arousing your interest sufficiently to make each one ask himself whether he could improve his business by installing a system of cost accounting, why I have accomplished all, for there is only one way to find out and that is by installing such a system, and I say without reservation that once the proper system is installed, the next question you will ask yourself will be, "How did I get along all this time without it?"

WOOD ALCOHOL—COÖPERATIVE CAUTION

By Charles Baskerville[1]

College of the City of New York, New York City

Received November 7, 1919

Unscrupulous persons have been selling mixtures containing wood alcohol, as such, or ethyl alcohol denatured with wood alcohol, as beverages. Coöperation of the chemical profession is sought to minimize this infraction of a law which seeks to safeguard people and yet provide industry with a most useful solvent and vehicle.

During the penumbra of prohibition the word *alcohol* has exercised a weird and unfortunate influence often times through failure to appreciate the significance of such qualifying words as "wood," "methyl," and "denatured." Numerous cases of blindness and even death have resulted through ignorance or the infamy referred to. The Commissioner of Internal Revenue has, consequently, issued the following notice:

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[1] Chairman Committee on Occupational Diseases, American Chemical Society.

To Collectors of Internal Revenue and Revenue Agents in Charge:

T. D. 2914, issued to-day and showing additional matter to be affixed to containers of completely denatured alcohol, is called to your especial attention.

Reports recently received in the Bureau establish that completely denatured alcohol is being used extensively for bathing and rubbing purposes. This is contrary to the law and regulations, and such uses cannot be tolerated, as the completely denatured alcohol is highly injurious to the skin and animal tissue.

It is also established that completely denatured alcohol is being sold by irresponsible dealers under circumstances as to assure them that it is being used for beverage purposes. Where it is so used for any length of time blindness inevitably ensues, and the continued use can only result in death.

Collectors should use every means at their disposal to make known to the public the dangers of either external or internal uses of completely denatured alcohol. Wherever collectors or revenue agents in charge hear of a misuse of completely denatured alcohol, a most thorough and careful examination should be made immediately and all the facts fully reported to the Commissioner for the infliction upon the responsible parties of the ultimate penalties provided by Law.

To Internal Revenue Officers and Others Concerned:

In view of the grave and extended abuses of the use of completely denatured alcohol reported, it is deemed necessary to print upon the labels affixed to wholesale and retail packages a further and more specific warning as to its use than is shown on the present required label.

In addition to the present matter on the labels there will be required on all new labels hereafter the printing, in large letters in red ink, under the skull and bones symbol, the word *poison*, and at the bottom of the label there will be printed the following statement:

> **Completely denatured alcohol is a violent poison. It cannot be applied externally to human or animal tissue without serious injurious results. It cannot be taken internally without inducing blindness and general physical decay, ultimately resulting in death.**

Until the present stocks of labels are exhausted, this additional matter may be affixed to the containers on a separate label pasted above the present required label.

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We chemists know that we daily handle poisons of various kinds, many far more dangerous than *wood alcohol*, and there are comparatively few evil results from their handling and use. People do not drink them. The medical profession administers daily to patients many substances that are poisonous except in the minute doses given. But in the case of *alcohol*, the "kicker" in drinks of quondam familiar kinds, means just that one desired fluid, hence attendant danger. We should do all in our power to protect those who use, and some likely to abuse, this important chemical, and thus incidentally avoid lurid appeals with consequent hampering legislation.

FOREIGN INDUSTRIAL NEWS

By A. McMillan, 24 Westend Park St., Glasgow, Scotland

A NEW MOTOR FUEL

According to a report in the *Times*, London, tests have been carried out on a new motor fuel, the invention of a South American Andrade. From the tests it was found that a car travelled over 30 miles on one gallon, and that, if the inventor's statements are true, a gallon can be manufactured for about ten cents. Experiments have been carried out in the presence of an experienced motor expert. The inventor claims that by mixing certain chemicals with water a liquid is produced capable of producing motor power. The chemicals may be introduced in the form of powder and minor experiments carried out are reported to be very encouraging.

NON-INFLAMMABLE TIMBER

A sample piece of yellow deal is sent by the Timber Fireproofing Company, of Fulham, treated by their oxylene fireproofing process, the use of which it is suggested, would avoid the risk of fires in houses built of wood. The process consists of submitting the wood in a closed cylinder to a steaming and vacuum treatment which removes the air and moisture in the pores of the wood and vaporizes the sap water. The wood is then impregnated under hydraulic pressure with a solution of fire-resisting chemicals which replace the elements driven out by the preliminary treatment. Finally the water of the solution is dried off and the chemicals in minute crystal form remain embedded in the fibers. The effect of this treatment is explained: that on the application of heat the crystals expand and form a glossy coating which excludes the oxygen of the air and prevents its combination with the wood, thus rendering flame an impossibility. The higher the temperature, the more the crystals expand, and though in time the chemical action of each crystal becomes exhausted and the wood becomes charred, fresh crystals come into play, and though the wood may eventually be charred completely through, no flame will be generated. Wood treated in this way does not differ in appearance from wood that has not been treated, and it is claimed that it does not corrode nails or screws, does not spoil paint or polish, does not warp, does not deteriorate, and is not affected by atmospheric conditions.

LINSEED OIL SUBSTITUTE

According to a German patent, the derivatives and substitution products of indene, in so far as they contain the double bond of the cyclopentane ring, *e. g.*, the oil products obtained by alkylating or aralkylating indene or indeniferous tar fractions in the methylene group are adapted to serve as substitutes for linseed oil on account of their miscibility with oil pigments and their property of drying in the air, especially in the presence of driers, to form glossy weatherproof lacquers which adhere firmly to the substratum and retain the pigments. For example, monobenzylindene (m. p. 33°–34°) can be transformed into varnish by the addition of 3 per cent lead-manganese resinate. A mixture of mono- and di-benzylidene with 3 per cent cobalt resinate or one of the xylylized indenes of indene oxalate is also suitable.

NEW WIRE ROD MILL

The new wire rod mill at Templeborough, near Sheffield, which has been put up by a combination of three firms, is now working. It is the only Morgan continuous rolling mill in England, and has an output capacity of 1,500 tons a week. On double strand working it produces two 300 lb. coils of wire rod every minute. Its fly wheel, 20 ft. in diameter, weighs 50 tons, and the leather belt, believed to be the largest ever made in this country, is 60 in. wide and $^5/_8$ in. thick.

DISTILLATION OF OIL SHALE IN GERMANY

Prior to the war, says a German contemporary, shale was worked on the Rhine provinces and near Reutlingen, but only one company was occupied in producing paraffin and mineral oils. From the bituminous shale which occurs near Messel (containing 40 to 45 per cent water, 6 to 10 per cent tar, 40 to 50 per cent residues), the following yields per ton of shale are obtained: 135 liters crude oil, together with 295 liters of ammonia water and 59 cubic meters of natural gas which is burned as fuel in gas engines or under the vertical retorts. During the war the oil shale deposits in South and North Germany have been investigated in regard to their yield but so far the results have not been published.

VARNISH FOR INSULATING MATERIAL

The choice of varnishes for coils, etc., forms the subject of a note in *Electrical World.* Slow-drying varieties being in general use, an important consideration is that the dielectric resistance increases directly with the length of baking or drying period, the slow varnish imparting the highest degree of insulation and flexibility and producing a tough, flexible film which may be depended upon for mechanical strength and extreme durability. Black varnishes are claimed to be better for work when a transparent coating is not absolutely essential because they produce a more flexible, highly insulating film than clear varnishes of the same class. Varnishes should not crystallize under prolonged vibration and their mechanical structure should be elastic and homogeneous. A table giving the characteristics, uses, drying time and solvents of several varnishes is also given.

PORTABLE ELECTRIC MOTORS

The main features of a series of motors built by Portable Electric Motors, Ltd., at Waldon, Essex, England, are their lightness in relation to their power, and the fact that they can be used on either direct or alternating current circuits. They are wound for 100 to 120 volts and 200 to 240 volts and for single-phase current with a frequency of 25 to 60 cycles. The standard size ranges from $^1/_{16}$ to 26 h. p. The weight complete of the $^1/_8$ h. p. size is $5^1/_2$ lbs. and of the $^1/_4$ h. p. size $9^3/_4$ lbs. They can thus be readily carried even by a girl worker and fitted with a flexible shaft they can be used for such pruposes as opening metal-lined cases, grinding small parts where great accuracy is required and buffing signs and brass work. Another form in which they are made is that of portable drills with either heavy or light type reducing gear; with a $^1/_4$ h. p. motor the heavy type, which weighs 17 lbs. complete, will drill holes up to $^1/_2$ in. diameter in steel, while the light type, weighing $14^1/_2$ lbs., will drill holes up to $^1/_4$ in. in steel and $^1/_2$ in. in hard wood or soft metal.

MACHINERY IN ITALY

A description of a factory which has been recently established in Turin for producing machinery for the weaving of woolen fabrics was recently given in the Italian press. It is stated that looms for weaving cotton used to be made in Italy but that machinery for woolen fabrics came from abroad and chiefly from Germany. A few months ago a factory was opened at Turin and has now an output of 4 looms per day, with the expectation of an increase. The quality is said to be excellent and orders have already been received from France, Belgium, and Brazil. Some difficulties have been experienced in getting raw material, but the iron castings which form the principal part of the looms are now supplied in Piedmont. Foreign competition is not feared since Germany is not at present in a position to produce or to deliver this class of goods, and in any case the government has promised protection to the new industry.

ALUMINUM IN NORWAY

Norway, says *Engineering*, is not well provided with aluminium minerals. There is practically no bauxite, kaolin or clays rich in aluminum, like those of Sweden and the continent which have been utilized in aluminum works with more or less success. The Norwegian clays do not contain more than 20 per cent of alumina, while Hungarian and Bavarian clays are said to come up to 30 per cent. There is a potash feldspar with 16 per cent aluminum but little has been done with it. It has been stated that the Norsk Elektrochemist Company was trying labradorite, containing 30 per cent of alumina, from the western provinces of the country. Labradorite is a feldspar, silicate of aluminum, sodium and calcium. The works are at Lysaker, and the Norsk Hydro Company, which makes nitric acid, is interested in it.

BRITISH IMPORT AND EXPORT OF CHEMICALS

The British Board of Trade have issued their annual statement of the trade with foreign countries and British Possessions for the year 1918. Included in this report are the values and in some cases the quantities of chemicals imported and exported during each of the years 1914 to 1918. The total value of imported chemicals, not liable to duty and exclusive of drugs, dyes and manures, was about \$102,494,924 in 1918 as against \$56,712,796 and \$16,721,600 in 1914. Imports of drugs, containing no suitable ingredient, were put down at \$14,000,024 in 1918, as compared with \$8,606,400 in 1914; dyestuffs, exclusive of tanning materials and dyewoods are given at \$14,430,064 in 1918 against \$8,215,844 in 1914; manures are given at 465,819 tons valued at \$7,813,768 in 1918 and 664,735 tons, worth \$5,188,856, in 1914. The values of the chemicals and chemical preparations, other than manures and medicines, exported in 1918 and 1914 were \$69,154,852 and \$9,424,620, respectively, while the value of exported manures is given at \$3,684,076 in 1918 and \$19,545,896 in 1914, and of medicines \$10,250,844 in 1918 and \$7,874,880 in 1914.

NEW INSULATING MATERIAL

According to *Engineering*, a new product suitable for use in electrical insulation is being obtained from the treatment of kelp in Australia. The moist precipitate is formed under pressure, after which it is hardened by treatment with formalin. The finished article is made by turning on the lathe, a process which is said to be perfectly successful, and a high polish is applied. The raw product is to be found in large quantities around the coast of Australia and in particular on the Tasmanian shores.

PAPER-MAKING FROM MEGASSE

A correspondent of the *Melbourne Age* writes as follows: The remedy for expensive bags is a simple one as there are thousands of tons of sugar cane waste (megasse) burned or thrown away every year in Queensland, New South Wales. This is one of the very best materials for making paper, corn sacks and wool packs, which latter may be made from paper at 30 to 40 per cent less than the cost of jute bags. This is a new industry with a great future before it and a company could readily be formed, machinery installed, and in less than 12 mo., Australia could be supplied with corn sacks, wool packs, binder twine and other articles at a minimum price, and made by Australian workmen.

SPHERICAL CRYSTALS

Having noticed more than 20 years ago that the alloys of tin and antimony yield what appear to be cubic crystals and those of tin and arsenic rhombohedral, flat plates, Dr. J. E. Stead made a trial to find how the metals would arrange themselves when the three elements were alloyed by fusion and the liquid allowed to cool slowly. The results, which he described before the Institute of Metals, were astonishing, for the crystals found in the matrix were in the form of incomplete spherical shells, the radii of which were minute or great in proportion to the time allowed for development. When solidification was effected in one second, the radius was less than $^1/_2$ min., but when it was protracted for an hour it was 5 min. or more. The most perfect structural arrangement of the crystals was obtained in an alloy containing 70 and 85 per cent of tin, 25 and 18 per cent of antimony and 4 to 5 of arsenic. Experiments with various proportions of the three elements showed that while about 2.5 per cent of arsenic was required to produce slightly curved crystals in the presence of 25 per cent antimony, even 0.5 per cent arsenic when the antimony was reduced to 3.75 per cent, yielded curved segments on the upper layers. The alloys are of no commercial value, though they might be used for the production of vases, buttons or paper weights.

SCIENTIFIC SOCIETIES

AMERICAN CHEMICAL SOCIETY ADVISORY COMMITTEE MINUTES

The Advisory Committee met at the home of President Nichols, New York City, at 5 P.M., November 28, 1919, with Messrs. Herty, Hesse, Nichols, Parsons, Stieglitz, and Whitaker present.

A communication from the National Foreign Trade Council was read regarding their convention in San Francisco, California, May 12 to 15, 1920. It was moved to refer this communication to Mr. H. S. Miner, chairman of the Committee on Foreign Chemical Trade in its Relation to our Merchant Marine, to Coöperate with the U. S. Shipping Board, with the suggestion that he arrange to have one or more members of his committee attend the meeting, adding two members to the committee from the Pacific Coast for this purpose if he deems it advisable.

On request of the editor of the *Journal of the American Chemical Society*, Dr. Stieglitz having resigned from the associate editorship, Dr. Lauder W. Jones and Dr. William C. Bray were added to the list of associate editors.

An invitation from the Bureau of Standards for the SOCIETY to be represented on December 8, 1919, at a conference on Industrial Safety Codes, was accepted, and Dr. Nichols, with Dr. Baskerville's concurrence, appointed R. B. Moore to attend this conference.

The Secretary was instructed to inform former German members asking for reinstatement, that reinstatement on request would follow the establishment of peace between the countries.

The Committee appointed C. G. Derick, William Hoskins, F. A. Lidbury, A. D. Little, Charles L. Reese, and C. P. Townsend associate editors to Dr. John Johnston, editor of the SOCIETY'S *Technological Monographs*. It was voted that Dr. Johnston's suggestion that of these six, two be elected for a term of three years, two for a term of four years, and two for a term of five years; and that after the end of the third year, two new members be elected each year for three-year terms and that they be ineligible for immediate reëlection, be approved. Dr. Johnston was asked to make the selection for the various terms by lot or otherwise as he deemed advisable.

It was moved that the nominees made by W. A. Noyes, namely, G. N. Lewis, L. B. Mendel, Julius Stieglitz and A. A. Noyes, be appointed associate editors with W. A. Noyes, editor of the *Scientific Monographs* of the AMERICAN CHEMICAL SOCIETY. It was voted that the salaries of John Johnston and W. A. Noyes, editors of the SOCIETY'S *Technological and Scientific Monographs*, begin October 1, 1919.

John E. Teeple was elected to the Board of Trustees for the AMERICAN CHEMICAL SOCIETY *Monographs*, in place of E. G. Love, deceased.

The following resolution of the Division of Pharmaceutical Chemistry was adopted:

> *Resolved*, That the Division of Pharmaceutical Chemistry recommend to the Advisory Committee the appointment of a committee consisting of one representative from each division and section of the SOCIETY to define the field to be covered by the respective divisions and sections. That the report of this committee after being approved by the Advisory Committee be published for the purpose of assisting authors in determining the division or section before which their papers should be presented, and for the guidance of officers of divisions and sections in preparing their programs.

President Nichols with the advice of the Committee appointed the secretaries of the various divisions to act on this committee with the suggestion from the Advisory Committee that it would in all probability be in the interest of the SOCIETY to give authors their choice of the Divisions in which they are to present their papers if the choice they make is at all reasonable.

The Advisory Committee formally approved the recommendation of the Division of Pharmaceutical Chemistry that Frank O. Taylor, George D. Rosengarten, and B. L. Murray be the SOCIETY'S delegates to the Pharmacopoeial Convention.

The resolutions of the Dye Section of the AMERICAN CHEMICAL SOCIETY passed at the Philadelphia meeting and referred to the Advisory Committee for approval were somewhat modified in wording, although not in import and were finally adopted as the resolutions of the SOCIETY in the following form:

> WHEREAS, The establishment of a complete, self-sustained coal-tar chemical and dye industry is a national necessity because of its well defined character as a key industry in our economic life, and,
>
> WHEREAS, This industry has a much deeper significance in that it constitutes a vital reserve both as to personnel and supplies for our Army and Navy in modern warfare, and
>
> WHEREAS, This industry is also essential for supplies of synthetic drugs for the health of the Army, Navy and general public in peace and in war, and
>
> WHEREAS, This country possesses an abundance of raw material for such an industry, ample capital, and chemists capable of solving the many scientific and technical questions involved, as evidenced by the splendid progress of the past three years, and
>
> WHEREAS, This initial period, with all of its attendant difficulties, has not yet been adequate to admit of the efficient production in domestic plants of all colors needed by American consumers, and
>
> WHEREAS, The greatly depreciated rate of exchange in that country which in the past has manufactured the bulk of the world's supply of dyes presents a new and threatening factor in all transactions of an international character;
>
> *Therefore, be it Resolved*, First, that we urge all Americans to stand loyally by the young industry which embodies such far-reaching potentialities of service and protection for our country;
>
> Second, that every needful safeguard be thrown around this industry by the Congress of the United States, especially through the imposition of effective import duties and the provision of a temporary licensing system along the general lines embodied in H. R. 8078 known as the Longworth bill.

The other resolutions passed by the Dye Section and by the joint meeting of the Division of Industrial and Engineering Chemistry, the Pharmaceutical Division, and the Dye Section, as printed on page 912 of the October issue of the *Journal of Industrial and Engineering Chemistry* were approved by the Advisory Committee.

The Chemical Reading Courses prepared by the Committee on the Preparation of a List of Chemical Texts for Libraries was presented to the Advisory Committee and was formally approved. The chairman was authorized to release these lists as he deemed advisable. The President instructed the Secretary to present to Mr. Hamor and through him to the members of his committee the thanks and appreciation of the Council for the excellent work done by the Committee.

A communication from Mr. W. A. Hamor proposing from time to time joint meetings of our local sections similar to the joint meetings which the American Society of Mechanical Engineers have been holding throughout the country was received and noted. The Secretary was instructed to inform Mr. Hamor that the Advisory Committee entirely approved of the idea but they felt that the initiative in matters of this kind should be taken by the local sections. In fact local sections have done this several times in the past and there is no objection to local sections arranging joint meetings whenever it seems desirable for them to do so.

A communication was received from the Polariscope Committee requesting the Advisory Committee to appoint a committee authorized to consult with officers of this Government and similar committees in other countries with the view of securing the adoption of an international normal weight for saccharimeters, the committee suggesting C. A. Browne, C. E. Coates, and G. W. Rolfe. The Advisory Committee approved of this suggestion and the committee was duly appointed.

A communication was received from Mr. Gerald L. Wendt requesting items of SOCIETY news for the Chicago Chemical Bulletin. The Committee voted that news items such as the election of officers, notices of meetings, etc., might be sent to the local bulletins of any of our sections by the editor of the *Journal of Industrial and Engineering Chemistry* with release date, such communications to be sent first by the Secretary of the SOCIETY to the SOCIETY'S official organ, the *Journal of Industrial and Engineering Chemistry*.

The following on recommendation of the editor were appointed the Advisory Board of the *Journal of Industrial and Engineering Chemistry:*

H. E. BARNARD
J. W. BECKMAN
A. D. LITTLE
A. V. H. MORY
C. L. REESE
G. D. ROSENGARTEN
T. B. WAGNER

The Advisory Committee, on recommendation of Editor E. J. Crane, passed the following vote:

That *Chemical Abstracts* be empowered to loan to members in good standing of the *American Chemical Society*, copies of current publications upon request; that each such request must be accompanied by twenty-five (25) cents for each issue requested to cover cost of packing, mailing and correspondence, and must further be accompanied by an undertaking on the part of the requesting member to replace such issue or issues, should they not be returned to *Chemical Abstracts* in good order, less reasonable wear and tear; *Chemical Abstracts* to notify the loaning member of receipt in good or bad order, as the case may be, of the loaned issue and then to close the transaction accordingly.

It was voted to recommend to the Board of Directors that a sum not to exceed $1,000.00 for traveling expenses be placed at the disposal of the President of the SOCIETY for the year 1920 for the purpose of visiting local sections of the SOCIETY, such trips to be made by arrangement with the President but only on condition that the section or sections visited pay one-half such expenses. It was suggested that local sections so far as possible arrange with the President or among themselves for joint meetings or continuous routing.

The Secretary was instructed to send to the councilors of the SOCIETY each month a separate reprint of the Proceedings, with the request that they read them carefully in order that they may be kept informed at all times on SOCIETY affairs. It is hoped that each councilor will keep these Proceedings in a separate folder so that he may refer to them readily on occasion.

The Committee then adjourned.

CHARLES L. PARSONS,
Secretary

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

The Twelfth Annual Meeting of the American Institute of Chemical Engineers was held in Savannah, Ga., December 2 to 6, 1919. A meeting of the Council and an informal reception were held on Tuesday evening at the Hotel DeSoto, the headquarters for the meeting.

The regular sessions were opened on Wednesday morning with an address of welcome by the Hon. Murray M. Stewart, mayor of the city of Savannah, who outlined the important commercial interests and industrial developments of Savannah, and gave a most cordial welcome to the chemical engineers. Mr. F. N. Smalley, of the Southern Cotton Oil Company, chairman of the local committee, welcomed the Institute and stated that this was the first scientific meeting ever held in Savannah.

Dr. Arthur D. Little, president of the Institute, presided at the business and other sessions of the meeting. Mr. Frank E. Dodge of the committee which canvassed the ballot for officers, reported the following elections: David Wesson, manager of the Technical Dept. of the Southern Cotton Oil Company, *President;* Henry Howard, of Boston, Mass., *First Vice President;* Prof. A. W. Smith, of Cleveland, Ohio, *Second Vice President;* Hugh K. Moore, chief chemist and chemical engineer of the Brown Company, Berlin, N. H., *Third Vice President;* J. C. Olsen, *Secretary;* F. W. Frerichs, *Treasurer;* Chas. F. McKenna, *Auditor;* C. T. Bragg, of Detroit, Mich., F. M. deBeers, of Chicago, Ill., H. S. Miner, of Gloucester City, N. J., C. L. Reese, of Wilmington, Del., and A. A. L. Veillon, of St. Louis, Mo., were elected *Directors*.

The Secretary reported a total membership of 344, with many applications pending. The publication of the *Transactions* had been delayed by the printers' strike. The Treasurer reported a satisfactory balance on hand with all bills paid.

After considerable discussion of the vital importance to the United States of the recently developed dye industry, the following resolution was unanimously adopted:

The American Institute of Chemical Engineers in convention assembled at Savannah, Ga., recognizing the importance of protecting the coal-tar industry and the dye industry in particular, not only to the industrial interests of the country in general, but also to its public health and the protection of the country in time of war, wishes to express itself in the following resolution:

That the American Institute of Chemical Engineers urges upon the United States Senate the importance of enacting the Longworth bill embodying the licensing plan protecting both the manufacturer and user of dyes.

This resolution was unanimously adopted and the Secretary directed to transmit same to Senator Penrose, chairman of the Finance Committee of the United States Senate.

Mr. Hugh K. Moore presented the plans which had been decided upon for the publication of Critical Compendia of Physical Constants, emphasizing particularly the necessity of raising between $100,000 and $200,000 for financing the undertaking. The following resolution was then adopted:

WHEREAS, Every industry, for its successful operation, depends upon an accurate knowledge of the properties of the materials it uses and produces, and the numerical values of these properties which are known as their constants and,

WHEREAS, During the war, it became evident that much of the published data on these constants was extremely inaccurate, entailing considerable loss in time and money, and it was found in many cases that data very much desired was not to be found in published records and,

WHEREAS, Up to now publication of such constants in tabular form has been mostly in some foreign language and consequently of limited availability and,

WHEREAS, Under allotment by the Interallied Council and the International Research Council, the National Research Council of the United States (an organization duly created by act of Congress), has decided that this deficiency could best be met by the compilation and publication in English of tables of constants which have been critically reviewed as to their accuracy and has decided that this could best be done by the appointment of a committee to act as trustees in charge of such compilations and as far as is necessary to have charge of the determination of such constants as have not already been published or determined and,

WHEREAS, The trustees so appointed were selected as representing the American Chemical Society, the American Physical Society, and the American Institute of Chemical Engineers, the representatives being, respectively, Julius Steiglitz, Edwin P. Hyde, and Hugh K. Moore,

Therefore be it Resolved, That the American Institute of Chemical Engineers in convention assembled heartily endorses this project and promises to the trustees its support in every way within its power.

Dr. L. H. Baekeland, chairman of the Patent Committee, reported satisfactory progress on the bills which have been introduced in Congress for the improvement of the patent system. These bills if passed will establish the Patent Office as an independent bureau, establish a United States Court of Patent Appeals and also increase the force and salaries of the Patent Office.

A number of papers were read on various phases of the development of southern chemical industries. President Little delivered an address on "Chemistry and the South," in which he emphasized the fact that the future of the South is in chemistry. The most important agricultural product of the South could be produced only by the application of the chemical fertilizers manufactured so largely in the South. The sulfuric acid industry, the turpentine and rosin, bauxite, cement, by-product coke, cottonseed oil, and other industries were pointed to as illustrations of what may be accomplished by the development of the natural resources of the South by means of chemistry.

Mr. David Wesson gave a paper on "The History and Development of the Cottonseed Oil Industry," illustrated by lantern slides.

Richard K. Meade in a paper on "Developments of Some Southern Industries," discussed the situation in the South so far as labor, transportation, power, fuel, and basic raw materials are concerned.

In a paper entitled "Some Developed Mineral Resources and Chemical Industries of the Southern States," A. M. Fairlie covered the development of the phosphate rock, sulfur, and pyrites deposits of the South and the manufacture of sulfuric acid and acid phosphate.

Maximilian Toch, in a paper on "Use of Rosin in Paint and Varnish," described the production of a varnish from rosin and china wood oil which is equal or superior to the best spar varnish.

"Some Developments in Chemical Engineering," by Mr. A. E. Marshall, showed how the chemical engineer should utilize more fully the experience of engineering in other industries.

Two papers were presented by Mr. Hugh K. Moore. One of these on "Accident Prevention in the Mill," gave an exhaustive treatment of this important subject. In the second paper, "An Analysis of the Explosion Process of Recovery of the Soda Salts from Black Liquor," Mr. Moore gave the results of a scientific study of the combustion of the black liquor of the sulfate pulp process which had resulted in the development of a remarkably efficient process of combustion of this liquor. Both of these papers were illustrated by lantern slides.

In a paper on "Recovery of Pyridene Bases at By-product Coke Ovens," by Frank E. Dodge and F. H. Rhodes, the authors gave details of a method for recovering these bases and showed that the ammonia produced would be very much purer on account of the absence of the pyridene bases.

Mr. Geo. A. Richter presented a paper on "Double Pipe Heat Exchangers," giving the results of experiments on the relation between the transfer of heat and the rapidity of flow of hot and cold liquids through straight and coiled pipes. A considerable increase in efficiency was shown by the coiled pipes.

Mr. F. C. Zeisberg in a paper on "Absorption Tower Packing Resistance to Gas Flow," showed how the efficiency of such towers could be calculated.

Mr. J. G. Dailey presented a paper on "Acid Electric Furnace Ferrotungsten," giving method of preparation and properties of this material.

The entertainment features of the meeting included an automobile trip around Savannah and vicinity, including Banventure, Thunderbolt and Isle of Hope, with a stop at Bethesda. Here an oyster roast had been arranged on the grounds of the first orphan asylum founded in the United States. The members of the Institute and their guests were accompanied by members of the Rotary Club and the local section of the AMERICAN CHEMICAL SOCIETY, making a company of about 150. A football game by the boys of the asylum was watched with great interest. The return trip was made *via* Vernon View, Montgomery and White Bluff, while some of the party returned to the Isle of Hope and inspected with great interest the unique terrapin farm of Savannah.

On Wednesday evening a smoker was held at Presslers Restaurant. The members of the local chemical society provided the entertainment, which included amusing songs descriptive of the president, secretary, and others, and instrumental and vocal music.

On Thursday a steamer trip was taken on the Savannah river and harbor. Members were surprised to see the extensive docks and shipping in Savannah harbor and were told that it ranked second to New York in commerce on the Atlantic Coast. A sawmill and paper pulp mill using the sulfate process was inspected with great interest and shipbuilding yards and one of the extensive cotton warehouses of Savannah, where cotton bales were subjected to high pressure before shipment, were also visited.

On Friday afternoon the plant of the Southern Cotton Oil Company was visited. The delinting machines were inspected with great interest as well as the cottonseed oil presses and methods of refining and production of large compounds. The plant is compact, very well managed and highly efficient. The Fertilizer plant of the American Agricultural Chemical Company was then visited. This plant produces acid phosphate and mixed fertilizers as well as sulfuric acid by the chamber process.

Friday evening the subscription dinner was held at the Hotel DeSoto. The coal conservation rules which limited the smoker to 10.30 P.M. did not apply to the dinner. Covers were laid for 100, including 35 ladies. The toastmaster, Mr. W. V. Davis, president of the American Trust Company, kept the company in the best of humor with his many humorous remarks. The speakers included President A. D. Little, who expressed the appreciation of the members of the institute of the hearty southern hospitality which had been accorded them, the Rev. Frederick F. Reese, Bishop of Georgia, Secretary Olsen and President-elect David Wesson. Mayor Stewart was present and expressed again the pleasure of the citizens of Savannah at having the Institute there for its meeting. Mr. Steve Harris spoke in a humorous vein, and Dr. H. E. Bassett, state bacteriologist, dwelt upon the work of this department.

On Saturday morning visits were made by small parties to the County Farm, where the manufacture of sugar cane syrup was shown. Another party saw the manufacture of crude turpentine and rosin.

The ladies were entertained at a theatre party on Wednesday evening, an auto ride and luncheon at the Golf Club on Thursday, and accompanied the men on the trip Friday afternoon to the plants of the Southern Cotton Oil Company and the American Agricultural Chemical Company. The attendance at the meeting was surprisingly large in view of the long trip to Savannah. The hospitable coöperation shown by the local chemical organizations was especially appreciated.

J. C. OLSEN, *Secretary*

PERKIN MEDAL AWARD

The Perkin Medal for 1919 has been awarded by the American Section of the Society of Chemical Industry to Dr. Chas. F. Chandler for his work on the standardization of kerosene. The committee in making the award called especial attention also to the work Professor Chandler, as head of the Chemistry Department of the School of Mines at Columbia University, has done in training men for the chemical industry.

The medal will be presented to Dr. Chandler, "dean of American chemists," at the regular meeting of the Society of Chemical Industry, American Section, at the Chemists' Club, New York City, on January 16, 1920.

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS

The Thirty-sixth Annual Convention of the Association of Official Agricultural Chemists was held at the New Willard

Hotel, Washington, D. C., November 17 to 19. Two hundred and sixty-four members and visitors were present. The usual reports of referees, associate referees and committees were presented and a number of special papers were read.

Dr. F. B. Power, of the U. S. Bureau of Chemistry, discussed a recently published paper by himself in collaboration with Mr. V. K. Chesnut on "An Improved Method for the Quantitative Determination of Caffeine in Vegetable Material."[1] The Association decided that this method should be made the subject of study in connection with the existing tentative methods.

Dr. H. W. Redfield, also of the U. S. Bureau of Chemistry, as a preliminary to the discussion of the referee on "Eggs and Egg Products," outlined briefly an extensive investigation which was carried on by himself and ten others in the Bureau of Chemistry for the purpose of developing reliable analytical methods for the detection of decomposition in eggs, and of correlating the analytical results obtained with the known quality of liquid and frozen egg products. He stated that the results of this work would soon appear in a bulletin of the U. S. Department of Agriculture.

Addresses were delivered by the President, Dr. P. F. Trowbridge, Agricultural Experiment Station, Agricultural College, North Dakota, on "A Plea for Greater Conservation of World Foodstuffs in the Fattening of Animals for the Market," and by the honorary president, Dr. Harvey W. Wiley, Washington, D. C., on "Problems of To-day and Their Bearing upon the Scientific World." The Secretary of the Association, Dr. Carl L. Alsberg, chief of the Bureau of Chemistry, Washington, D. C., announced the resumption of the publication of the *Journal of the Association of Official Agricultural Chemists* and said that the next number would appear about November 25, 1919, and that the "Book of Methods," containing the tentative and official methods of analysis of the Association, would be available for distribution some time in February 1920. Prolonged discussion of papers made the meeting one of the most interesting and profitable in years. The following officers were appointed for the ensuing year: *President*, H. C. Lythgoe, State Department of Health, Boston, Mass.; *Vice President*, W. F. Hand, Agricultural College, Agricultural College, Miss.; *Secretary-Treasurer*, C. L. Alsberg, Bureau of Chemistry, Department of Agriculture, Washington, D. C. Additional members of the Executive Committee are C. H. Jones, University of Vermont, Burlington, Vt., and W. W. Skinner, Bureau of Chemistry, Washington, D. C.

The names of members of committees and of referees appointed may be secured through the secretary.

C. L. ALSBERG, *Secretary*

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[1] *J. Am. Chem. Soc.*, **41** (1919), 1298.

NICHOLS MEDAL AWARD

The jury of award of the William H. Nichols Medal has decided upon the contribution by Dr. Irving Langmuir on "The Arrangement of Electrons in Atoms and Molecules," published in the *Journal of the American Chemical Society*, as being the outstanding feature of the publications of the SOCIETY during the past year. The medal will, therefore, be conferred upon Dr. Langmuir at the March meeting of the New York Section of the SOCIETY.

CALENDAR OF MEETINGS

American Association for the Advancement of Science—Seventy-second Meeting, St. Louis, Mo., December 29, 1919, to January 3, 1920.

American Ceramic Society—Annual Meeting, Hotel Bellevue-Stratford, Philadelphia, Pa., February 23 to 26, 1920.

American Chemical Society—Fifty-ninth Meeting, St. Louis, Mo., April 1920.

American Electrochemical Society—Spring Meeting, Boston, Mass., April 8 to 10, 1920.

NOTES AND CORRESPONDENCE

MEETING OF THE STOCKHOLDERS OF THE CHEMICAL FOUNDATION, INC., ON DECEMBER 2, 1919

The Chemical Foundation, Inc., offices were crowded with personal representatives of the companies owning stock in that organization. It was a thoroughly representative group of chemical-industrial interests, and much enthusiasm was aroused in the work of the Foundation.

The following subscribers were present:

Ault & Wiborg	Messrs. Wiborg and Holt
Barrett Company	Mr. Jayne
Central Dyestuff & Chemical Co.	Mr. Metz
Consolidated Color & Chemical Co.	Mr. Metz
John Campbell & Co.	Mr. Whaley, Miss Simmons
Dow Chemical Company	Mr. Pardee
Dye Products Chemical Co.	Messrs. Simons and Lowenthal
E. I. du Pont de Nemours & Co.	Messrs. Harrington, Bolton, and Patterson
General Chemical Company	Mr. Wigglesworth
Grasselli Chemical Company	Messrs. Grasselli and Cashman
Heller & Merz	Mr. A. Merz
G. H. Morrill	Mr. Anthony
Merck & Co.	Mr. Murray
H. A. Metz Laboratories	Mr. Metz
Monsanto Chemical Co.	Mr. McCartney
Merrimac Chemical Co.	Mr. Howard
Naugatuck Chemical Co.	Mr. Lang
National Aniline & Chemical Co.	Messrs. Baldwin, Kalish, and Atherton
Roessler & Hasslacher Chemical Co	Mr. Rigney
Union Carbide & Carbon	Dr. Townsend
Electric Boat Co.	Mr. Dawson
Aniline Dye & Chemical Co.	Mr. Fieldhouse
Permutit Co	Mr. Norton
Lindsay Light	Mr. Sinai
American Cellulose & Chemical Co.	Mr. Larkin
Lehn & Fink	Mr. Plaut
American Chemical Society	Dr. Herty
National Ammonia	Messrs. Guernsey and Atwood
Parke-Davis	Mr. Smith
C. E. Bischoff	Mr. Kuhl
Mallinckrodt Chemical Co.	Mr. Bary
Zinsser & Co.	Mr. Zinsser
Eastern Drug Co.	Mr. West
Powers-Weightman-Rosengarten	Mr. Rosengarten
Kelly-Springfield Co.	Mr. Seaman
Abbott Laboratories	Dr. Abbott
Peerless Color Co.	Mr. Cornelison
Commercial Research	Mr. Sutherland
Winthrop C. Durfee	Mr. Durfee
Jos. Bancroft & Son	Mr. Bancroft
Upjohn & Co.	Mr. Upjohn
E. R. Squibb & Sons	Dr. Anderson
Johnson & Johnson	Dr. Kilmer
F. E. Atteaux	Mr. Atteaux
Hercules Powder Co.	Mr. Norman
Irvington Smelting & Refining	Mr. Barker
Baker & Co., Inc.	Mr. Colby
American Platinum Works	Mr. Englehardt
C. Engelhardt	Mr. Newcomb
Hanovia Chemical Co.	Mr. Robinson
American Cotton Oil Co	Mr. Lamb
Lonsdale Co.	Mr. Langdon
Rhodia Chemical Co.	Mr. White
General Bakelite Co.	Dr. Baekeland
Citro Chemical Co.	Mr. White
Borne-Scrymser	Mr. Waring
Mt. Hope Finishing	Mr. Williams
United Piece Dye Works	Mr. Blum
Heyden Chemical Co	Mr Chamberlain
Armour Fertilizer Works	Mr. Riley
Schieffelin & Co.	Dr. Schieffelin
John Lucas	Mr. Gilmore
E. C. Klipstein & Sons	Mr Klipstein and Major Sill
R. H. Comey & Co.	Mr Parsons

There were also present:

Douglas I. McKay, Vice President of the Chemical Foundation
H. E. Bateman, Asst. to Vice President of the Chemical Foundation
S. A. Tucker, Chief Chemist of the Chemical Foundation
Joseph H. Choate, Jr., General Counsel of the Chemical Foundation
Ramsay Hoguet, Patent Counsel of the Chemical Foundation
E. T Connelly, Manufacturing Chemists' Association

In the absence of President Garvan, Vice President Douglas I. McKay opened the meeting with a brief address, setting forth the purposes of the Foundation and giving a brief history of its activities to date. He explained further, that it was the desire of the officers of the Foundation to be guided in all of their actions by the constant advice of the leaders in the industry. For that reason it was proposed to establish a Chemical Foundation Advisory Committee for which the following constitution was proposed:

CONSTITUTION AND BY-LAWS
CHEMICAL FOUNDATION ADVISORY COMMITTEE

ARTICLE I

NAME

The name of this Committee shall be the CHEMICAL FOUNDATION ADVISORY COMMITTEE.

ARTICLE II

The Chemical Foundation Advisory Committee is established, subject to the supervision and control of the Board of Directors and President of the Chemical Foundation, Inc., to promote in all lawful ways the interests, objects and purposes of the Chemical Foundation, Inc., to coöperate in an advisory capacity with the Foundation in the determination of its general policies and of its policies regarding the forms, limitations and distribution of licenses under its patents, and to render such other services to the Chemical Foundation, Inc., as may be deemed beneficial to the Chemical Foundation, Inc., and to the Public Safety and Welfare.

ARTICLE III

ORGANIZATION OF THE COMMITTEE

SECTION 1—The Advisory Committee shall consist of the President and Vice President of the Chemical Foundation, Inc., a representative of the American Dyes Institute, and a representative of the Manufacturing Chemists' Association of the United States, to be respectively chosen by each Association; the Chairman of the Section Committees, and not to exceed five committeemen at large, to be chosen by the President of the Chemical Foundation, Inc.

The Advisory Committee, shall supervise and direct investigation of any and all matters which the Board of Directors or President of the Chemical Foundation, Inc., may refer to it, and shall report thereon to said Board of Directors or President, shall appoint such special sub-committees as it may deem necessary, and may abolish the same, and shall have such other powers and duties as may be given to it from time to time by the President and Board of Directors of the Chemical Foundation, Inc.

SECTION 2. MEETINGS OF THE ADVISORY COMMITTEE—A meeting of the Advisory Committee shall be held immediately after the Annual Meetings of the Section Committees, as hereinafter provided for. Regular monthly meetings shall be held at 2:30 o'clock P.M. on the third Wednesday of each month, and special meetings may be held at the call of the President or Vice President of the Chemical Foundation, Inc., or by request in writing to the Secretary signed by three members of the Advisory Committee. At least five days' notice of such meetings shall be given to each member of the Advisory Committee. Five members of the Advisory Committee shall constitute a quorum.

ARTICLE IV

OFFICERS

SECTION 1—The officers of the Advisory Committee shall be a Chairman, a Vice Chairman, who shall be respectively the President and Vice President of the Chemical Foundation, Inc., and a Secretary, who shall be elected annually by the Advisory Committee at its annual meeting. The Secretary shall hold office for one year and until his successor shall have been elected and shall have accepted office. Any vacancies in office shall be filled by the Advisory Committee. The Secretary need not be a member of the Committee.

SECTION 2—The Chairman shall preside at all meetings of the Advisory Committee. He shall be a member, *ex officio*, of all Sections and all committees and shall perform such duties as are necessarily incident to his office.

In the absence or disability of the Chairman his duties shall be performed by the Vice Chairman. The Vice Chairman shall be a member, *ex officio*, of all Sections and all committees.

SECTION 3—The Secretary shall keep a record of the proceedings of the Advisory Committee and of all other meetings of which a record shall be deemed advisable by the Advisory Committee. It shall be the duty of the Secretary to issue notices for all meetings of the Advisory Committee. He shall perform such other duties as may be delegated to him by the Advisory Committee.

ARTICLE V

ORGANIZATION OF SECTIONS

SECTION 1—The stockholders of the Chemical Foundation, Inc., shall be divided into the following sections for the purpose of assembling in groups of like or kindred interest:

1—Dyes and Intermediates
2—Pharmaceuticals and Medicinal Chemicals
3—General Chemicals and Fertilizers
4—Textiles, including Dyers and Finishers

Additional sections shall be formed from time to time when in the opinion of the President or Board of Directors of the Chemical Foundation, Inc., there is a sufficient number of stockholders of like or kindred interest to justify their formation.

Each stockholder shall designate the section into which assignment is desired, and shall be so assigned. No stockholder shall be assigned to more than one section except upon approval of the President or Vice President of the Chemical Foundation, Inc.

SECTION 2—Sections shall be represented by a section committee of not less than three elected by and from the membership of each section. The Chairman and Vice Chairman of the Advisory Committee shall be *ex-officio* members of all sections and all committees.

SECTION 3—Each section may adopt its own rules and regulations provided such are not inconsistent with the Constitution and By-laws of the Advisory Committee.

SECTION 4—Each section shall elect its section committee at the time of the annual meeting, or at the time of any special meeting of the stockholders called for the purpose. Section Committees shall have power to elect their own chairman and to fill vacancies. No person shall be chairman of more than one section committee. Each chairman of a section committee shall be *ipso facto* a member of the Advisory Committee.

ARTICLE VI

SECTION MEETINGS

SECTION 1. ANNUAL MEETING—The annual meeting of all sections shall be held immediately following the annual stockholders meeting of the Chemical Foundation, Inc., and at the same place.

SECTION 2. SPECIAL MEETINGS—The Secretary shall call a special meeting of any section or section committee whenever directed to do so by the Advisory Committee or whenever requested in writing to do so by five or more members of the particular section. Each such request in writing shall state the object or objects for which the meeting is desired, and no object not so stated shall be acted upon at the meeting.

SECTION 3. NOTICE OF MEETING—At least 14 days' written notice or 7 days' telegraphic notice of the annual meeting or of any special meeting shall be sent by the Secretary to each member. Notice of each special meeting shall set forth the object or objects for which it is called.

SECTION 4. QUORUM—A quorum at any annual or special meeting of any section shall be not less than three members in person or by proxy, unless and until such section shall by resolution otherwise provide. Less than a quorum may adjourn any meeting for a period not longer than twenty days.

SECTION 5—Each member shall be entitled to one vote, irrespective of the amount of stock of the Chemical Foundation, Inc., held, and may vote in person, or by proxy, provided the proxy be duly executed in writing within two months prior to the meeting at which it is presented for use. A proxy given for any meeting shall, unless notice of revocation is delivered to the presiding officer, hold good for adjournments of that meeting.

ARTICLE VII

RESIGNATION AND WITHDRAWAL

Any member may withdraw from any section by giving written notice of resignation to the Secretary, and any member who ceases to be a stockholder of the Chemical Foundation, Inc., shall *ipso facto* cease to be a section member.

ARTICLE VIII

AMENDMENTS

The Constitution and By-laws may be amended at any meeting of the stockholders of the Chemical Foundation, Inc., by a vote of two-thirds of the members present in person or by proxy, provided a copy of the amendment or the substance thereof shall have been given in the notice calling the meeting.

The Advisory Committee may amend the Constitution and By-laws at any meeting by a vote of two-thirds of the members present subject to ratification at the next succeeding meeting of the stockholders of the Chemical Foundation, Inc.

The following amendments to this constitution were adopted:

1—There shall be one additional section known as Metallurgical Section, or Section 5.

2—There shall be one additional section known as Unclassified Section, or Section 6.

Following the adoption of the constitution the stockholders were given an opportunity to signify to which section they desired to belong and a recess was declared for the purpose of organizing the several sections.

The following chairmen of the various sections were elected:

SECTION 1—JAMES T. PARDEE, The Dow Chemical Co., Midland, Mich.

SECTION 2—DR. W. J. SCHIEFFELIN, Schieffelin & Co., 170 William St., New York.

SECTION 3—MR. P. S. RIGNEY, Roessler & Hasslacher, 100 William St., New York

SECTION 4—MR. BLUM (Temporary), United Piece Dye Works, 132 Madison Ave., New York.

SECTION 5—THOMAS C. DAWSON, Electric Boat Co., 11 Pine St., New York.

SECTION 6—S. S. NORTON, Permutit Co., 440 Fourth Ave., New York.

These chairmen, and a representative of the Dyes Institute and the Manufacturing Chemists' Association, together with five members to be appointed at large by the President, constitute the Advisory Committee to the Chemical Foundation, Inc.

Mr. Choate and Mr. Hoguet then explained to the members the situation in regard to the Foundation's title to the patents, and both expressed the opinion that, whether the Peace Treaty was ratified or not, the title to the patents owned by the Foundation was clear.

The question of increasing the membership in the Foundation was also discussed. At the time of the meeting there were 139 subscribers to the stock, of whom sixty-seven were present.

A FATAL LABORATORY ACCIDENT

The circumstances of the accident which resulted in the death of Mr. E. C. McKelvy, of the Bureau of Standards, as recorded in another column, have been issued by the Chemical Society of Washington.

At the time of the accident Mr. McKelvy, Mr. C. S. Taylor, and Mr. D. H. Simpson were working together on the same apparatus, determining the freezing point of ammonia. The apparatus consisted essentially of an unsilvered Dewar cylinder container, 20 cm. high and 9 cm. inside diameter. The cylinder contained a glass tube in which the ammonia was frozen, and in which was fitted a platinum resistance thermometer, a mechanical stirrer which was driven by a small ball motor about a foot away, and a copper coil into which liquid air was siphoned in small amounts, about 1 cc. at a time. Most of the rest of the space in the cylinder was filled with petroleum ether (about 600 cc.) used as a contact liquid or bath. Petroleum ether was used because other mixtures become either very viscous or else cloudy at low temperatures. The petroleum ether was cooled to 0° C. before introduction into the Dewar container. About twenty seconds before the accident, at which time the temperature of the bath was —30° C., Mr. Taylor and Mr. Simpson, who were working within a foot of Mr. McKelvy left the room and entered the adjoining room. At that time Mr. McKelvy was cooling the bath by siphoning small amounts of liquid air into the copper coil. A loud explosion was heard, and about eight or ten seconds later Mr. McKelvy, with his clothes in flames, was standing under the shower bath at the entrance to the room. Mr. Taylor, aided by Mr. Yurow, immediately turned on the water to the shower bath, and at the same time Mr. Simpson wrapped him in the woolen fire blanket hanging immediately over the shower bath. The fire was out in less than five seconds after Mr. Taylor entered the room.

Mr. McKelvy was at once taken to the hospital, where in spite of all possible care and attention, he died on the following day, as a result of the very extensive burned areas involved.

The exact cause of the accident is not known. Mr. McKelvy said that there was an explosion and everything in the vicinity was afire. The same apparatus had been used in the same way several times before without any signs of trouble. It was designed to be absolutely safe. Several possible explanations have been offered since the disaster:

1—The Dewar flask collapsed and the glass rubbing together produced a spark.

2—The Dewar collapsed and threw petroleum ether into the motor commutator.

3—A static spark ignited the petroleum ether-air mixture in the container and then broke the container.

4—A petroleum ether-air mixture was ignited by the motor commutator.

THE EXAMINATION OF THE COLLEGE TRAINED CHEMIST FOR GOVERNMENT SERVICE

Editor of the Journal of Industrial and Engineering Chemistry:

One of the unfortunate things about the war was that, when so many things had to be done, there was not time to do them all well. One is especially struck with this in reading the illuminating statistical article of W. T. Cotton[1] on "The Examination of the College Trained Chemist for Government Service."

But now that peace is here, or (*senatu volente*) nearly here, is it not time to distinguish a makeshift from the real thing, and to recognize the necessary superficiality in every makeshift? It would certainly be doing Dr. Cotton an injustice to infer that he seriously believes that mere magnitude, mere figures, are what count in giving a good chemical education. And yet, assuming that the Government wants in its chemists something more than an average of mediocrity, one is fairly driven by parts of his article to the conclusion that two of the essentials in a college or university for the providing of an adequate chemical education (and why any other kind?) are:

(*1*) *The offering in the catalog of a large number of hours of chemical courses.*

(*2*) *The possession of a large chemical faculty.*

Apparently the classification of educational institutions by the Civil Service Commission was based on these two factors. Yet the absurdity of the first as a criterion is laid bare by the author on the next page of his article where he condemns the padding of college catalogs; and as for the second—somewhere, if I remember correctly, certain radical individuals have dared to point out the importance of the ratio of the number of instructors to the number of pupils.

One great teacher had only twelve students, Socrates had not many more, and in the old days it used to be said that Mark Hopkins on one end of a log and a boy on the other made a college. But in these days it is all changed; study the catalogs of 550 institutions, tabulate the data, and—presto—the sheep are separated from the goats.

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[1] THIS JOURNAL, 11 (1919), 1142.

We graduates of the smaller colleges had thought that the intensity factor in education was as important as the quantity factor—that quality counted; and, for example (if I may be excused for bringing in my own Alma Mater), some support was found for this belief in the fact that for a number of years Amherst College, with a chemical faculty of but three, did not send a single post-graduate student to Columbia who did not win a university or an approximately equivalent fellowship; and she sent her fair share of students.

It was undoubtedly inevitable that in the exigencies of war some such method of selection as that described should become necessary, and it is wise that it should now be published. But, unless we are mad about figures and bigness, let us recognize that systems such as this do not furnish reliable criteria for peace-time use.

366 Montgomery Street
Brooklyn, N. Y.
December 12, 1919

M. L. Hamlin

PLATINUM THEFTS

Between October 3 and 6, 1919, two sets of platinum electrodes for Kimley electrolyte apparatus and one 20 cc. platinum crucible were stolen from a desk drawer in the balance room of the Habirshaw Electric Cable Co., Yonkers, N. Y. The loss amounts to between $350 and $400.

WASHINGTON LETTER

By J. B. McDonnell, Union Trust Building, Washington, D. C.

The American dyestuff and coal-tar chemical industry has laid its case before the Senate and now is awaiting the action of that body on the Longworth dye bill, embodying the much-fought-over import licensing system.

During the whole of last week a dyes subcommittee of the Senate Finance Committee conducted hearings on the Longworth bill and some time this week will report to a meeting of the full Committee. An effort will be made to have a measure reported from the Committee to the Senate before the Christmas recess, and action upon it there is planned for early in the new year.

Condensation of the testimony of witnesses which required a week in the giving must necessarily disregard many points in favor and in opposition which were made during the hearings. Much the same ground was gone over before the Senate Committee as was covered before the House Ways and Means Committee. The opponents of the licensing feature shifted their attack somewhat, and the burden of their testimony was a complaint against the War Trade Board and its Dyes Advisory Committee. Led by Colonel John P. Wood, of Philadelphia, the opposition appeared in force, Colonel Wood occupying several hours before the committee, reading steadily from a prepared statement.

The hearings actually were but the culmination of a fight which has been waged for months and will be continued in the future. The large committee room in the Senate office building was crowded. It was indicative of the interest in the proceedings that there was little straggling—the committee room was crowded before the hour set for the resumption of the hearings after each recess. The interest at times was tense and flared up in but poorly concealed ill-temper. There were opponents of the licensing system who undoubtedly were absolutely sincere in their objections. There were others who obviously were thinking of nothing else than their own selfish interests; and yet others who professed to be altruists solely, and standing to lose little if the system was enacted into law, opposed it nevertheless because of their solicitude for dye consumers, among which, however, they were not numbered.

Unwittingly, in their attacks upon the War Trade Board for its carrying out of its licensing power, the opponents of the bill laid the foundation of one of the strongest shots which were delivered by supporters. The story told the committee by Dr. Charles H. Herty of his trip to Europe as the American representative to obtain German dyestuffs, was keenly interesting to the committee, but has already been told in these pages. Dr. Herty several times approached to the brink of disclosures but contented himself with definite statements that had it not been for activities in this country German dyes already would be in this country.

The full force of his statements was brought to light when Francis P. Garvan, Alien Property Custodian and president of the Chemical Foundation, Inc., appeared before the committee—the last witness to be heard—and charged that the dye importing firm of Kuttroff, Pickhardt & Company was responsible for the delay in shipments of German dyes which had been arranged for. It was disclosed publicly for the first time also that the head of the German chemical cartel, von Weinberg, had attempted to avoid the bargain he entered into with this country through Dr. Herty.

> "We would have the dyes on our docks in New York for the relief of all the industries of America—and you must remember that they were asked to submit them—we spread it as far as we could—every need that they would have for six months," Mr. Garvan told the committee. "The allocations were obtained; the order was sent at an expense of some twenty-five hundred dollars. Dr. Herty had the signed word of von Weinberg. All was safe until an agent of von Weinberg in this country turned the key And America cannot to-day get the dyes she needs."
>
> Picking up a paper before him he read:
>
> "November 14, 1919
>
> To Anilin Fabrik, Ludwigshafen:
>
> We fully expect modification Government regulations which will permit us to confirm our orders. This will enable you to maintain your position that all goods to this country outside reparation goods should come to us.
>
> Kuttroff and Pickhardt"
>
> "When they got that cablegram to the effect that our method of getting it through the State Department and the Reparations Commission had fallen through," Mr. Garvan continued, "then they cabled back five days after that cablegram was sent: 'Sorry we cannot renew your option. von Weinberg.'
>
> "Kuttroff and Pickhardt seeing that the licensing system was about to be a success and seeing that America was about to be freed of any annoyance for her dyes for the next six months, and desiring to hinder this legislation, to have the licensing system appear a failure, sent that personal word. And immediately back comes the telegram: 'We cannot fill the order, the option cannot be extended.'"

A letter which had been sent out by the above-mentioned firm to dye consumers, urging that they oppose the licensing system, was then read to the committee by Mr. Garvan.

While it was not brought out in the hearing, it was learned that immediately upon receipt here of the cable from von Weinberg, head of the German cartel, efforts to bring pressure to bear upon the German industry were made through the State Department. Government officials insisted that the option had not expired, but had been exercised. The success of these efforts is indicated in a message from von Weinberg to Dr. Herty received to-day and at once communicated to government officials here that the German cartel was ready to proceed as agreed upon and only details remained to be worked out with the representative of the Textile Alliance, Mr. H. G. Stephenson, who is now in Paris. Officials here see no further delay, with the exception of possible transportation difficulties, in the delivery of German dyestuffs in this country.

That further light may be thrown upon the present-day activities of former German dye agents in this country was indicated by Mr. Garvan who stated that he had other cables which had been sent to Germany by the Kuttroff-Pickhardt firm, which had not yet been decoded. Mr. Garvan's testimony was delivered amid silence. There was no effort at oratory. There were no fine rolling phrases. His intense earnestness was reflected in the intense interest of his hearers. His eloquence gripped his audience, not with admiration for his delivery but with the picture he vividly painted them, and one expected for a moment to hear a burst of applause when he had concluded.

After outlining the scope and activities in this country of the German chemical industry, and its vital relation to us, its espionage work, and how it was used in an effort to sway our foreign policy, Mr. Garvan continued:

> "Now it is our contention that in accordance with the general scheme of Germany's attempted commercial supremacy, this institution has gone on in the form decided on long ago, until there is one institution, the I. G., irrespective of whether there was a war or not—and I ask you gentlemen to consider that if the war had not come, with its alarm and its instruction, what condition the textile and dependent industries in this country would have been in on the date in 1916 when all the chemical industries in

Germany, having crushed out every other dye industry in the world, were united under one head, von Weinberg.

"In other words, you are faced to-day with a choice between two licensing systems, one inaugurated by our own Government on behalf of the domestic manufacturers, the other licensing system in the hands of Herr von Weinberg, who is at the head of the combined German dye works of to-day. In other words, not a textile manufacturer in this country can receive one pound of dye except at the personal will of von Weinberg, except such as we have provided for through the Reparations Commission. That, in my opinion, is what confronts us.

"The dye agencies here were the whole structure of the German espionage system. There is not a phase of chemical life that these agencies over here would not make weekly and monthly scientific and careful reports to Germany on. I could give you samples of them in the failure of legislation, business, and everything else in which they had a hand. They were soldiers in the army of Germany. The intent of Germany, of the great chemical industry, was carried out by them. If they have changed, of course, we are all grateful; but, I will say, if they have changed they will not continue to be agents for the I. G., because the I. G. has not changed; nor have its purposes changed, which are to control as far as they can the industry of the world.

"It is my contention that it is a most short-sighted policy to let the inconveniences of the licensing system, which are at their peak now—and we are providing for a six months' supply—interfere with our proper consideration of this matter now.

"Gentlemen of the committee, you can pass all the laws you want to pass, and make them mountain high, and it will not reach the situation. The agent can say I have not enough dye. I have only enough for those people who buy all their dyes from us. Is that a crime? On the other hand, if there is some system by which the market of America may be open for the investor who has invested his money and made a dye, that is all we are after. What the method is I do not think anybody cares.

"Gentlemen, this thing has burnt into our minds throughout the past two years, but I do not think anything brought it to my mind so clearly and distinctly as did the fact that after the armistice airships flew over the sea; and during the same week that those ships flew between England and America, the Department of the Interior exhibited in a little vial a new gas that they had discovered but had not put into the war, and it was asserted by our army officials that five airplanes could carry over New York enough gas in one night to annihilate the 5,000,000 inhabitants of that city. Where are we going to get any protection from such gas in the future? There is only one protection possible. That is for a country that might send some airships over here with that gas to know that we can send back ships the next night and annihilate the people or the city that manufactured it.

"We know that this was an industrial war. This chemical business was the cause, largely, of the war. The Germans would never have gone into the war without a consciousness of a feeling of the superiority of their chemical industry. They went into the war, in fact, or got ready for the war the day in 1913 when they had perfected their nitrate processes and were independent.

"And so it is now—their only hope of penetrating into the business of this country in the ruthless manner of the past is through the chemical industry.

"We felt that we would like to be a part in the taking of the forces of science, developed by them—but which they have only turned to the desolation and destruction of mankind—and placing it in the hands of what we believe is a higher and purer civilization; and see if we cannot, out of the terrible mess of this war, do something constructive with the same scientific forces which heretofore have been devoted to nothing but evil.

"It is only to give American principles, character and energy a chance that we ask you to hold these people off until we get our education. Then we will meet them without any tariff."

The importance of the dye and coal-tar chemical industry to the national defense of the country was outlined to the country by army and navy officers when the hearings were first begun. Then followed other men nationally known in their work who told of the educational and scientific side of the industry, and of its value to the health of the world. Dye manufacturers told of their problems which have been overcome and those which still must be successfully met. Conditions in Germany were described by Dr. Herty and Major Theodore W. Sill, who was a member of a military commission which entered the occupied area immediately after signing of the armistice. Then followed the opposition to the licensing system, composed principally of consumers from the Philadelphia district, and dye importers.

Perhaps one of the most important announcements made to the committee during the course of the hearings was a statement by Irenee du Pont, head of E. I. du Pont de Nemours and Company, that his dye company already had developed eight vat dyes and were only waiting until they had perfected them in quantity production before they placed them on the market. These new vat dyes, he said, probably would be ready for the market about the middle of January, perhaps earlier. This is going the previous announcement much better, as it was stated some time ago that it was hoped by the company to have four vat colors ready for the market in January.

Criticism of the War Trade Board, its Advisory Committee on Dyes, the principle of import licensing, and the actions of the American dye manufacturers during the time they had the protection of the war were voiced by witnesses who appeared against the licensing system.

In answer to criticisms by opponents of the bill the Advisory Committee of the War Trade Board and the Textile Alliance filed briefs showing that every delay in the obtaining of needed German dyes was due to influences outside of these bodies. Mr. Joseph H. Choate, Jr., also filed a brief reviewing critically the testimony of the several opponents of the bill.

The need of consumers for vat dyes was recognized, and the committee was told that every effort now was being made to supply that need with imports of dyestuffs from Germany. Franklin W. Hobbs, chairman of the Dyes Advisory Committee of the War Trade Board, which had come in for much criticism, in a statement made to the committee declared that it was obviously the purpose of these criticisms to defeat a permanent licensing board. Criticisms for this purpose, he said were unjust, and the same difficulties would not be faced by consumers in obtaining dyes through a permanent licensing body as was the case with the temporary War Trade Board machinery.

The dye industry went before the committee with all the prejudice of the committee members against the proposal they favored. They presented their case; and the license opponents presented theirs. It is certain that compared from practically all angles the opponents made not so good a showing by far as did those who supported licensing of imports. When the hearings were closed much of the disfavor with which committee members looked upon the licensing feature had been removed. Willing to enact protective legislation before they heard the explanation of the necessity for licensing, they were convinced of one thing at least—that tariff alone would not properly protect the industry, and that the licensing system was not quite so bad as had been painted.

The committee took half of one day from the dye industry during the week to hear the case of the kindred industry of chemical glassware and scientific and surgical instruments, and this bill, which also has been passed by the House, will receive early consideration after the holiday recess of Congress.

December 15, 1919

INDUSTRIAL NOTES

The British government was recently declared by Justice Sir John Sankey, of the King's Bench Division, to possess no power to prohibit the importation of certain goods and that, therefore, its proclamation to this effect was invalid and illegal. The judgment is considered one of the most important ever rendered against the government. The case decided concerned the importation of pyrogallic acid from the United States, the acid having been seized on its arrival.

The Manufacturers Oil & Grease Co., Cleveland, Ohio, has begun construction on a two-story plant estimated at $50,000.

Initial plans for stimulating organized accident prevention work among the chemical and allied industries were laid at the first monthly meeting of the Chemical Section of the National Safety Council which was held at the Engineer's Club in New York City on November 17, 1919.

The Fisher Fertilizer Co., Atlanta, Ga., which recently filed articles of incorporation with a capital of $250,000, is planning the erection of a plant for the manufacture of fertilizers.

The Royal Netherlands Salt Industry, a newly-formed company, is about to bore for salt in the provinces of Gelderland and Overyssel, Holland. The preliminary expert investigation indicated the possibility of a billion tons or more of salt underlying the soil of those provinces. If the quality is satisfactory and production is fast enough, Holland will be independent in regard to salt. Its consumption of salt is about 170,000 tons a year, all of which has hitherto been imported.

The Durham Hosiery Mills, of Durham, N. C., have arranged for the erection of a completely equipped modern dyehouse, together with the necessary preliminary survey and study of present dyeing operations.

At the annual shareholders' meeting of the Badische Anilin und Soda Fabrik there was considerable discussion about the proposal to move the headquarters of the corporation from Mannheim across the Rhine to Ludwigshafen. A dividend of 12 per cent was declared as compared with 20 per cent for the previous year. The management reported that the first ten months of 1918 had been quite satisfactory as far as the activity of the factory was concerned, but the income from sales had not kept apace with the increased costs of operations. The last two months of the year, however, brought disaster. In February 1919, bonds to the extent of 50,000,000 marks (about $11,900,000 at par) were issued by the Badische, the principal object of which was to provide funds for factory extension and improvement.

It is announced by the director of sales that the War Department has consummated the sale of the Explosives Plant at Nitro, W. Va., to the Charleston Industrial Corp., Charleston, W. Va. The explosives plant and other facilities owned by the War Department were recently offered for sale under informal bids and the property was awarded to the Charleston Industrial Corporation on its bid of $8,551,000.

The National Research Council and the American Ceramic Society have established a joint committee for promoting the investigation of scientific problems underlying the ceramic industry, especially by founding a series of research fellowships whose holders shall devote their attention exclusively to these problems.

The Natural Dyewoods Co., Ltd., New York, completed in November the largest individual contract of recent years for dyewoods in the West Indies, whereby this company acquires contract rights to 12,000 acres of timber in northwest Haiti. This tract was estimated in 1917 to contain 160,000 tons logwood, 20,000 tons lignum vitae and possibly 10,000,000 ft. of mahogany, cedar, and other cabinet woods. Analysis indicates extract solution equal, both in dyeing strength and twaddle content, to the best wood from Tampico, Mexico, and Jamaica.

That the American dye trade sees the urgency of putting America on a solid basis of independence in this industry is evidenced by the incorporation of numerous new works and the expansion of many of the smaller works which arose as a war measure and are now settling down to regular production. Among these are the Crystal Piece Dye Works, Inc., New York, which has increased its capital from $5,000 to $50,000; the Spooner Dye Works, New York, incorporated by J. and J. Cuchiara and A. Granatelli, capital $10,000; the Magic Products Corporation, New York, incorporated by J. C. Berrien, H. Freidman and J. Kahn, capital $10,000; the Narlinton Extract Dye & Chemical Co., incorporated under the laws of West Virginia by C. A. Weagher, G. W. Hunley, Jr., and J. A. Dennison, with a capital of $200,000; The Erie Dyeing Company, Cleveland, Ohio, recently incorporated under the new name, the Erie Dyeing & Processing Company, with a capital of $10,000; the Superior Dye Works, Brooklyn, N. Y., which will erect a $10,000 plant; the Universal Aniline Dye & Chemical Co., Milwaukee, Wis., which plans the construction of a plant in the South Milwaukee district; the Utica Dyeing Co., Utica, N. Y., which will erect an addition to its plant; and the Amalgamated Dyestuff Chemical Works, Newark, N. J., which plans an $8,000 extension to its plant.

Remarkable developments of the textile industry are under way in Chattanooga, Tenn., where it is estimated $25,000,000 are invested in the numerous plants. The Thatcher Spinning Co., controlling the Standard Processing Co., will build another addition, increasing its investment nearly $3,500,000. The United Hosiery Mills Corporation will build cottages and additions to the Madeline Hosiery Mills, increasing its investment $2,250,000. The Richmond Hosiery Mills and the Chattanooga Knitting Mills now have an investment of $2,000,000, the increase to be spent for improvements in their plants. President Garnet Andrews established the first textile mill in Chattanooga twenty-three years ago, with a capital of $4,500. The Dixie Mercerizing Co., recently organized with $750,000 capital, will soon announce site for its plant. The Southern Hosiery Mill and the Davenport Hosiery Mills are other new enterprises. The annual volume of business for these textile industries is estimated at $50,000,000, and their operatives number about 15,000 in Chattanooga alone.

Dyes and dyestuffs to the amount of $1,425,983 were exported by American manufacturers during September, the largest buyers being China, Japan, Canada, and British India in the order named; Aniline dyes brought $785,497, logwood extract $83,481, and all others $557,005.

The National Pulp, Paper & Cordage Co., Inc., has been incorporated under the laws of Delaware by Rodney Hughes, S. S. Bagot and John W. St. Pierre, of New Orleans, La., with a capital of $500,000 to deal in dyestuffs, among other things.

Secretary of War Baker has recommended to Representative Kahn, of California, a merging of the nitrate enterprises under Federal control, which Mr. Kahn has introduced. The bill authorizes the Secretary of War to appoint five persons to organize the United States Fixed Nitrogen Corporation, including the nitrate fixation plants of the Government at Sheffield and Muscle Shoals, Ala., the Fixed Nitrogen Research Laboratory at Washington and auxiliaries of those plants, together with any other property belonging to the Government and under control of the President or of the Secretary of War, that they may deem advisable to convey to the new corporation, to acquire and establish laboratories and experimental plants that may be necessary to assist in furnishing to the Government and others at all times nitrogen products for military and other purposes in the most economical manner and of the highest standard, to acquire American or foreign patents, to sell and export products not needed by this Government or by American fertilizer manufacturers or by other Americans. A draft of the proposed bill accompanied Secretary Baker's recommendation. The War Department seeks an additional appropriation of $12,000,000 for enlargement of this plan. This was one of the fundamental reasons for establishing the plant at Muscle Shoals where in peace times it will be of enormous value in increasing the supply of nitrates for agriculture, while in war times it would be an unsurpassed location for the production of nitrates for explosives.

A recent report on the phosphate rock industry, published by the *Geological Survey*, states that the total quantity of phosphate marketed in this country in 1918 was slightly under 2,500,000 tons, valued at more than $8,000,000, twice as much as was produced in all other parts of the world combined during that year. Florida alone produced over 2,000,000 tons, with Tennessee also a big producer. The report emphasizes the need of phosphate as one of the three minerals most necessary to make agricultural industry more productive and prosperous, and its ample deposits in this country do much to offset the lack of the other two requisite minerals for agricultural purposes, potash and nitrate, most of which are imported.

A paper presented by Otto Kress, of the University of Wisconsin, at the meeting of the American Pulp and Paper Mill Superintendents Association, states that the dyestuff industry is directly related to about twenty distinct American industries represented by 11,037 establishments with an invested capital of $2,530,200,000 and an annual production valued at $2,631,390,000, and giving employment to 1,070,400 people.

The American Consul General at Shanghai, in a recent report, states that the American dye trade with Shanghai gives promise of assuming commercial importance, particularly if prices admit of competition, especially with the Swiss dyes. Imports of aniline dyes in Shanghai in 1918 rose to more than twice the amount of 1917, a considerable part being imported by parcel post.

The American Agricultural Chemical Co., New Jersey, has been chartered, with a capital of $1,500,000, for the manufacture and sale of fertilizers, fertilizer products, sulfur, pyrites, nitric acid, fluorine, and chemicals of all kinds.

The Lumpkin Mining Company will develop Georgia's fullers' earth deposits near Lumpkin. They will erect a $100,000 fireproof building and install machinery to produce a daily output of 100 tons.

The Victor Chemical Works, Chicago, has bought a twenty-two acre site at Nashville, Tenn., for the establishment of a $600,000 chemical plant to be operated in connection with Tennessee phosphate rock developments.

The Union Seed & Fertilizer Co., Memphis, Tennessee, has begun construction of one of the largest crude oil mills in the South. Cottonseed oil is to be the first product, but it is learned that the company is to have a general analytical laboratory there and will have the largest and most complete chemical plant in the South.

The Connecticut Metal and Chemical Company is building factories at East Berlin, Conn., and has already moved its chemical research department from New Britain to East Berlin.

The Pacific Whiting Company is preparing to develop property in Nevada and to produce calcium carbonate on a large scale. This company owns an old lake bed which contains a variety of precipitated salts and minerals.

An explosion of 10,000 pounds of black powder at the plant of the du Pont Powder Co., at Wayne, near Paterson, N. J., caused the death of two men. The explosion occurred in the finishing building where the glaze is put on the powder.

Turkey has only one modern dyeing establishment, the Oriental Carpet Manufacturing Co., a British plant, in Smyrna. The government textile factories usually maintain dyeing departments of their own. Small dye shops exist all over Asia Minor, and German synthetic dyes are generally used, though natural indigo still predominates. There is also a German establishment in Constantinople which includes dyeing works with mechanical power and a chemical laundry.

The National Aniline and Chemical Co., Inc., announces the production of two new dyes, Erie yellow Y and wool blue C B. The first is a direct color practically identical with the pre-war chrysophenine and is not only valuable for cotton but also for wool and union goods. The second is identical with the pre-war azo wool blue C, similar to azo acid blue B, and is of special value in dyeing worsted goods with silk effects. This is the first bright blue of a reddish shade manufactured by this company.

Eugene Suter & Co., 120 Broadway, New York, specializing in fertilizer materials, chemicals, oils and dyes, have established a branch at 60 Gartenstrasse, Basle, Switzerland.

Lehigh University, Bethlehem, Pa., is erecting a three-story extension to its chemistry and chemical engineering laboratory. The addition will include an assaying room, organic laboratory and a quantitative analysis laboratory, and is estimated to cost about $75,000.

The Acme White Lead & Color Works, Detroit, Mich., has awarded contract for the building of a four-story plant in Hamtramck, Mich.

The New York City Board of Education, through the Bureau of Vocational Activities, has established a textile school under the direction of W. H. Dooley. Two courses are offered, a two-year course in general textiles, and a two-year course in applied textile design. The school was founded by the Upholstery Association of America. A complete experimental dye laboratory has been donated and part of the equipment has been given by textile manufacturing firms and dye interests.

Sodium sulfate estimated at 6,000,000 tons has been discovered in the Blue Mountains, Saskatchewan, on a branch of the Canadian National Railway. The salts are said to be 98 per cent pure, needing no refining and worth upwards of $20 per ton. Limestone has also been found in the district, promising the possible manufacture of sodium carbonate.

The California Ink Co., San Francisco, has taken over the business of G. D. Graham and the California Aniline and Chemical Company, and is preparing to enlarge its manufacturing facilities. Ownership of the latter company makes it independent of foreign dyes and chemicals. This company supplies about 90 per cent of the newspapers west of Denver with ink and has a large export trade.

The Kentucky Color & Chemical Co., Louisville, Ky., has been reorganized and construction work is under way at an estimated cost of $70,000. An annual output of 2,000,000 pounds of colors for manufacturing paints and varnishes, sprays, insecticides, and general chemicals is estimated.

The Atlantic Dyestuff Company, Boston, Mass., recently announced a new dye which they are putting out and which is known as "Atlantic Blue B Extra Concentrated." This dye possesses the properties usually found in the sulfur blues, being very fast to washing, light, fulling and cross-dyeing. Its shade is hardly altered by an after-treatment with bichrome.

The Glidden Co., Cleveland, Ohio, manufacturers of paints, varnishes, etc., has acquired the Campbell Glass & Paint Co., operating plants in St. Louis and Kansas City, Mo., and the Mound City Linseed Oil Co., St. Louis, Mo., for a price approximately $900,000.

The new crop of Egyptian cottonseed for England was scheduled to arrive in Hull, England, early in December, the amount from all sources being estimated at 400,000 tons, about two-thirds of Britain's pre-war importation. The deficiency in cottonseed during recent years has been compensated for in part by increased imports of refined cotton oil from America and by increased home production of edible oils and fats from oil-nuts. A comparison of the total imports for the period January to September 1918 with those for the same period, 1919, shows an increase of 250,524 long tons in 1919. England's oil-seed and oil-nut crushing industry is now greater than Germany's was before the war.

The Heyl Laboratories, Inc., announce the removal of their laboratories and plant from Chicago to New York City, which step was taken in view of the necessity of increasing their capacity and the fact that nearly all of their raw material is made in the East. Their capital has been increased from $10,000 to $60,000 and they have equipped a new plant solely for the production of acriflavine, for the manufacture of which they have the only license in the United States.

The Director of Sales, War Department, invites informal proposals from chemical manufacturers, dealers and distributors to market on a commission basis the surplus stocks of manufacturing chemicals, acids and allied products held by its several bureaus, which should be addressed to the Raw Materials and Scrap Section, Office of the Director of Sales, Room 2507, Munitions Building, Washington, D. C. The date of opening bids is January 5, 1920. The following is an enumeration of the principal products which will be embraced in the proposed contract, and the approximate surplus of each:

Mixed Acid 17,138,000 lbs., Nitric Acid 829,000 lbs., Oleum 6,153,000 lbs., Sulfuric Acid 43,800,000 lbs., Acetic Acid 65,000 lbs.

Absorbent Oils 81,300 gals., Calcium Carbide 636,000 lbs., Diphenylamine 100,000 lbs., Naphthalene Flakes 511,000 lbs., Magnesia Powder 21,000 lbs., Potassium Chlorate 10,500 lbs., Solvent Naphtha 28,200 gals., Caustic Soda 109,000 lbs., Methyl Acetate 500,000 lbs., Miscellaneous Oils 350,000 gals.

The National Research Council has formed a special committee on food and nutrition problems, composed of a group of the most eminent physiological chemists and nutrition experts of the country, which will devote its attention and activities to the solution of important problems connected with the nutritional values and most effective grouping and preparation of foods, both for human and animal use. Special attention will be given to national food conditions and to comprehensive problems involving the coördinated services of numerous investigators and laboratories. The committee, with the support of the Council, is arranging to obtain funds for the support of its researches, and will get under way, just as soon as possible, certain specific investigations already formulated by individual committee members and subcommittees. These include studies of the comparative food values of meat and milk and of the conditions of production of these foods in the United States, together with the whole problem of animal nutrition; the nutritional standards of infancy and adolescence; the formation of a national institute of nutrition; and other problems of similarly large and nationally important character.

The Cocoanut Products Corporation, Baltimore, Md., has completed a large plant there and is preparing to begin production for use in the manufacture of cocoanut meal cakes, drugs, soap, explosives, butter, and lard. This company has a 52,000 acre plantation in the Philippines.

PERSONAL NOTES

Dr. Arthur Lachman, a prominent chemist of the California Section, whose address is Holbrook Building, San Francisco, California, disappeared on December 11, leaving no clue, disappearance supposed to be due to temporary dementia and accompanying loss of identity. All members are asked to bear this in mind in the hope that some clue may be found.

Mr. Hugh Byron Gordon has resigned his position as assistant professor of chemistry at Rutgers College and is now with the the U. S. Conditioning Co., of New York City.

Mr. Ernest R. Schierz has resigned as chemist in the engineering department of the National Carbon Co., Inc., of East St. Louis, to accept a position as instructor in the chemistry department of the University of Wisconsin, Madison, Wis.

Mr. Henry M. McCance, for the past seven years chemist for the Pacific Guano and Fertilizer Co., of Honolulu, Hawaii, has recently accepted a position as research chemist with the Virginia-Carolina Chemical Co., Richmond, Va.

Mr. C. E. King, formerly of the University of North Dakota, has been made professor of physiology and pharmacology in the School of Medicine, University of Alabama, Mobile, Ala.

Mr. Harold C. Urey, formerly with the Barrett Company, Frankfort, Pa., recently accepted a position as instructor in chemistry at the State University, Missoula, Mont.

Miss Ruth Thomas has resigned as research associate in organic chemistry at Massachusetts Institute of Technology, Cambridge, Mass., to accept a position on the editorial staff of THIS JOURNAL.

Dr. H. E. Barnard, a Director of the AMERICAN CHEMICAL SOCIETY, a member of the Advisory Board of THIS JOURNAL, and for the past fourteen years chemist to the State Board of Health of Indiana, State Food and Drug Commissioner, State Commissioner of Weights and Measures, and Federal Food Administrator for Indiana during the period of the war, has resigned his official position with the State to become director of the newly-founded American Institute of Baking, at Dunwoody Institute, Minneapolis, Minn.

Mr. Ernest C. McKelvy, chief of the physical chemistry section of the chemistry division of the Bureau of Standards, died November 19, 1919, as a result of burns sustained in an accident in his laboratory on the previous day. Mr. McKelvy was born in Upper Sandusky, Ohio, May 9, 1884, and was educated at Western Reserve University. He later studied at Purdue University and the University of Wisconsin and received his M. A. from the latter university in 1908. Mr. McKelvy had been connected with the staff of the Bureau of Standards since his graduation. He was a member of the Alpha Tau Omega Fraternity, the University Club of Washington, the Washington Academy of Sciences, the American Association for the Advancement of Science, and secretary of the local section of the AMERICAN CHEMICAL SOCIETY. Through his long association with Washington activities he had made a host of friends who grieve at the untimely interruption of a life so full of promise.

Professor Grinnell Jones has severed his active connection with the Tariff Commission in order to resume his duties as a member of the faculty of Harvard University, Cambridge, Mass. He is still retained, however, on the staff of the Tariff Commission in a consulting capacity.

Dr. Harlan L. Trumbull and **Mr. Webster N. Jones**, who have been conducting investigations for the B. F. Goodrich Company, in Kent Laboratory, University of Chicago, since last April, are now attached to the staff of the research laboratory of the company in Akron. Associated with them in this work is **Mr. Henry Howard**, formerly with Newhall and Company, of Seattle, Wash.

Mr. Robert S. Bly, formerly in the Chemical Warfare Service and later in the laboratories of the Florida Wood Products Company, of Jacksonville, Fla., as research chemist, is at present in the chemistry department of Northwestern University, Evanston, Ill., assisting and doing work under Professor Lewis for the Ph.D. degree.

Miss Mary Wetton has resigned as instructor in chemistry at Iowa State College, Ames, Iowa, to accept a similar position at the University of Washington, Seattle, Wash.

Dr. Arthur W. Nixon and **Dr. Jerome J. Morgan** have been appointed to the faculty of chemical engineering of Columbia University. Dr. Nixon, specialist in explosives, was appointed associate professor of chemical engineering and Dr. Morgan, formerly assistant professor of chemistry at Stevens Institute of Technology, was appointed assistant professor of chemical engineering.

Mr. Arthur C. Eaton, formerly employed by the Lord Brothers Company, Portland, Me., is now with the East Coast Fisheries Products Company, Rockland, Me.

Mr. Max Latshaw resigned his position as chemist of the by-products laboratory of the Zenitti Furnace Company, Duluth, Minn., to accept a part time assistantship in the school of chemistry at the University of Minnesota, Minneapolis, Minn., and at the same time to pursue graduate work.

Mr. Harlan A. Depew, formerly research physical chemist of the Firestone Tire and Rubber Company, Akron, Ohio, is now in the employ of the New Jersey Zinc Company, Palmerton, Pa., where he is engaged in experimental work on rubber compounds.

Mr. Ben H. Nicolet, formerly at the Mellon Institute, University of Pittsburgh, Pittsburgh, Pa., working on various industrial fellowships and later connected with the Chemical Warfare Service laboratory in Paris, where he had charge of the work along organic chemical lines, with the rank of Captain, has become assistant professor of chemistry at the University of Chicago, Chicago, Ill.

Dr. Louis E. Wise has severed his connections with E. I. du Pont de Nemours and Company, where he held a research position at their Jackson Laboratory, Wilmington, Del., and has accepted the position of professor of forest chemistry in charge of the department of forest chemistry at the New York State College of Forestry, Syracuse University, Syracuse, N. Y.

Dr. Jean F. Piccard, recently connected with the University of Chicago, Chicago, Ill., has returned to Switzerland.

Dr. John Tapan Stoddard, professor of chemistry at Smith College since 1878, died at Northampton, Mass., on December 8, 1919.

Messrs. **E. L. Stephens**, president, **L. W. Stephens**, vice president, and **J. F. Stephens**, secretary and treasurer, three brothers who gave up their growing business to enlist for service in 1917, have returned to Chicago where they are reëstablishing their business, known as the Stephens Chemical Works.

Mr. Charles G. Miller, until recently assistant chemist for the Ajax Rubber Co., Racine, Wis., has accepted a position as chief chemist for the McClaren Rubber Co., Charlotte, N. C.

Mr. E. H. Kellogg has left Brown & Company, pulp and paper manufacturers, Berlin, N. H., where he was employed as chemical engineer, to join the sales department of the Burrell Technical Supply Co., of Pittsburgh, Pa.

Mr. Russell W. Stovel, recently Lieutenant-Colonel, Engineers, U. S. Army, has been appointed consulting engineer for Westinghouse, Church, Kerr & Company, Inc., New York City.

Lieut. J. H. Becque, who has been stationed at the U. S. Chemical Plant, Saltville, Va., has received his honorable discharge from the Army and has accepted a fellowship at the Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

Dr. Paul V. Faragher, formerly associate professor of chemistry at the University of Kansas, and more recently fellow at the Mellon Institute, is now connected with the experimental laboratory of the Research Bureau of the Aluminum Company of America, New Kensington, Pa.

Mr. William M. Corse has resigned his position as technical superintendent of the Ohio Brass Co., Mansfield, Ohio, and has accepted a position as general manager of the Monel Metal Products Corp., Bayonne, N. J.

Mr. Wm. M. Bovard has severed his relations as chief chemist at the Emerson Laboratory, Springfield, Mass., to become manager of technical service with the Package Paper and Supply Corp., Springfield, Mass.

Mr. B. E. Long, recently engaged in working out cost data on the manufacture of alcohol and other possible gasoline substitutes for some banking interests in the U. S., is now engaged as chief chemist and superintendent of fabrications at the sugar factory "Josefita," near Havana, Cuba, where he will remain until about next June.

Professor L. J. Cross, of Cornell University, who is absent on leave during the first term, 1919–1920, is studying the problem of the utilization of the waste fruit products of the Pacific Coast states, which work is being done in an experimental plant at Hood River, Oregon.

Mr. Harold Gray, who has been on the research staff of Eli & Company of Indianapolis, Ind., for the past four years, is now on the research staff of B. F. Goodrich Co., Akron, Ohio, in the organic development department.

Mr. Robert G. Dort recently left the engineering division of the U. S. Air Service to take a technical position with the Standard Textile Products Company, New York City.

Mr. Robert A. Fisher, previously a student in the Graduate School of Ohio State University, is chemist for the gasoline department of the Ohio Fuel Oil Co., Blue Creek, W. Va.

Mr. M. Landon has left the employ of the Koppers Company of Pittsburgh, where he was employed as a benzol operating engineer, supervising the starting of benzol plants built by them, and has become operating superintendent of the Columbian Carbon Company's gasoline absorption plant, Smithton, W. Va.

Mr. R. K. Brodie has been transferred from the position of industrial fellow at the Mellon Institute of Industrial Research to the chemical department of the chemical division of Procter and Gamble Company. Ivorydale, Ohio.

Mr. Peter G. Pirrie, who has for some years past been active in the baking and milling industry as a chemical engineer, and recently on the staff of the Siebel Institute of Technology of Chicago, has accepted the position of chief of the trade and service laboratories of the American Institute of Baking at Minneapolis, and will also act as associate instructor on the staff of the Wm. Hood Dunwoody Industrial Institute of that city.

Mr. O. J. Stewart, formerly instructor in chemistry at the New Hampshire College, Durham, N. H., is connected in a similar capacity with the University of Kentucky, Lexington, Ky.

Dr. Louis J. Gillespie, for the past six years investigator in the Department of Agriculture, Washington, D. C., is professor of physical chemistry at Syracuse University, Syracuse, N. Y.

Mr. Arthur Given, who has served as Lieutenant in the Ordnance Department, was recently discharged but remains in the Ordnance Department in civilian capacity as chief of propellant production at Picatinny Arsenal, Dover, N. J.

Mr. Daniel H. Rupp, formerly assistant chemist to Mr. J. E. Goodell, chemist for the City of Lancaster, Pa., and later in the Sanitary Corps, on duty in the Sanitary Engineering Section, Division of Sanitation of the Surgeon General's office, Washington, D. C., is now with the City of Ravenna, Ohio, as chemist in charge of the water purification works.

Mr. G. Francis Gray, who served in the Signal Corp in the Radio Development Section, as well as representing the Signal Corp on the Research Information Committee of the National Research Council, acting as liaison officer with the Naval Consulting Board, has become associated with the engineering department of the National Aniline and Chemical Company, New York City.

Mr. Harry Gordon has resigned his position as research chemist of the Kistler Leather Company, Lock Haven, Pa., and has accepted a position in the research laboratory of the Eastman Kodak Co., Rochester, N. Y.

Mr. Herman C. Lythgoe, director of the Food and Drug Division of the Massachusetts State Department of Health, was elected president of the Association of Official Agricultural Chemists at their recent meeting in Washington, D. C.

Mr. Paul Smith, formerly chemist with E. Rauh & Sons Fertilizer Co., of Indianapolis, Ind., now has a commercial laboratory at 122 E. Ohio St., Indianapolis, Ind.

Mr. B. B. Brandt has severed his connections with the Union Dye & Chemical Corp., of Kingsport, Tenn., and is now associated with the Dicks, David & Heller Co., Chicago Heights, Ill., where he will be engaged in introducing a new line of dyes and intermediates.

Mr. Frank A. Rohrs, formerly with the coke and by-product department of the Steel & Tube Co. of America, Wisconsin, has been engaged as research chemist for Kirkman Soap Manufacturing Co., New York City.

Mr. M. H. Webster, for the past six years closely associated with the development department of Murray & Nickell Manufacturing Co., Chicago, has been appointed chief chemist for the Colombia Alkaloid Co., of Houston, Texas.

Mr. Stephen R. Morey, who returned from France some time ago and who has been discharged from the Service after having served 15 months, now holds the position of general manager for the National Reduction Corp., Calvert, Ala.

Dr. Eric K. Rideal, a graduate of Cambridge University and the University of Bonn, more recently a Captain of the Royal Engineers in the British Army, has been appointed visiting professor of physical chemistry at the University of Illinois for the current year.

Mr. Clyde L. Voress has resigned as chief chemist for the Ohio Fuel Supply Co., and has accepted a position with the United Natural Gas Co., Bradford, Pa., to carry out a line of plant experimentation.

Mr. Richard Franchot, formerly in the Chemical Warfare Service and discharged from that service about a year ago, is vice president of the Ferro Chemicals, Inc., Washington, D. C.

Dr. George Heyl has resigned as secretary of the Heyl Laboratories, Inc., New York City, and has become vice president and technical director of that concern.

Mr. John C. Cannon, who was recently discharged from the Service, has accepted the position of assistant in the chemical research department of Warner Klipstein Chemical Co., of Charleston, W. Va.

Mr. I. Grageroff, with the Canadian Explosives Company, Ltd., for the last four and a half years, recently left that company to start in business with Mr. Chas. F. Papazoni, and is engaged in consulting work in industrial chemistry, being located at Los Angeles, California.

Mr. G. S. J. Dalton, formerly assistant superintendent of the Mansfield Tire & Rubber Co., Mansfield, Ohio, has accepted a position as superintendent of the Columbus Tire & Rubber Company, Columbus, Ohio.

Mr. David F. Gould, formerly assistant chemist in the research laboratory of the Mexican Petroleum Corporation, Destrehan, La., is now research chemist with the chemical department of the Barrett Company, Frankford, Pa.

Dr. Harold Hibbert has been appointed assistant professor of chemistry in the post-graduate research department of Organic Chemistry, Yale University, New Haven, Conn.

Mr. E. R. Clark has resigned his position in the textile section of the Bureau of Standards, Washington, D. C., to continue similar work in the central laboratory of the Standard Textile Products Co., New York City.

Mr. George S. Trump recently left his position as chemist with the Lycoming Foundry and Machine Company, of Williamsport, Pa., to take a position as instructor in foundry chemistry at Wentworth Institute, Boston, Mass.

Mr. Harry R. Beard has resigned as research chemist at the Fixed Nitrogen Research Laboratory, Washington, D. C., and has accepted a place as instructor in chemistry at the University of Wisconsin, Madison, Wis.

Mr. E. M. Bissonette, formerly with E. I. du Pont de Nemours & Co., at their dye plant at Deepwater Point, N. J., where he was in charge of the manufacture of naphthalene intermediates, is now with the Atlantic Refining Co., Pittsburgh, Pa., in charge of some refinery operations.

Mr. George N. Fisher has changed his business relations from that of chemist for the Certain-teed Products Corporation, Niagara Falls, N. Y., to that of chemist for the General Chemical Co., East St. Louis, Ill.

Dr. Edward E. Smith, formerly chemist in the food control laboratory of the Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C., is now chief chemist for F. W. Stock & Sons, flour millers, of Hillsdale, Michigan.

Mr. Arthur L. Stern has resigned from his position as research engineer with the Pennsylvania Trojan Powder Co., of Allentown, Pa., and is now with the Max Marx Color and Chemical Co., of Irvington, N. J.

Mr. Louis A. Butts is now general field clerk of the Ohio Cities Gas Co., located at Oilton, Okla., having formerly been instructor of chemistry and physics in the township high school, Farmer City, Ill.

Mr. T. S. Huxham, who was formerly with the Condensite Company of America in their research laboratory at Bloomfield, N. J., has charge of the laboratory of the Ramapo Ore Co., of Rockland County, New York.

Mr. W. Albert Noyes, Jr., A.B., from Grinnell College, whose special field is chemistry, has been awarded a fellowship by the Society for American Fellowships in French Universities.

Mr. Lewis O. Bernhagen, who recently received his discharge from the Army is at present assistant sanitary engineer of the Texas State Board of Health, Austin, Texas.

Mr. J. S. Laird has resigned from his position as assistant professor of chemical engineering in the University of Michigan, Ann Arbor, Michigan, and has joined the research department of the Jeffrey-DeWitt Co., Detroit, Michigan.

Dr. C. A. Brautlecht is now professor of chemistry and head of the department of chemistry and chemical engineering at the University of Maine, Orono, Me.

Mr. W. Rowland Collins, formerly with the Wilckes Martin Wilckes Co., Camden, N. J., is now chemist for the Royal Baking Powder Co., at their Chicago factory.

Professor G. Vauthier has been appointed professor of chemistry at the French University, Shanghai, China.

Mr. E. R. Lederer, formerly connected with the Galena Signal Oil Co., and later with the Home Oil Refining Co., of Texas, is now identified with the Atlantic Gulf Oil Corporation, with headquarters in New York.

Mr. L. J. Pletcher, formerly with the Texas Company, in their research laboratory at Port Arthur, Texas, has taken a position with Wilson & Co., in their laboratory at the Union Stock Yards, Chicago.

Mr. Leonidas R. Littleton, formerly chief chemist for the Mathieson Alkali Works, Inc., Saltville, Va., has accepted a position as chemist in the research laboratory of the National Aniline and Chemical Co., Buffalo, N. Y.

Mr. W. A. Bridgeman has left his position as chemist and purchasing agent for the Teagle Company, of Cleveland, to become general manager of the Wilbur White Chemical Co., Oswego, N. Y.

Mr. D. Franklin Fisher, formerly connected with the Bureau of Chemistry, U. S. Department of Agriculture, New York, N. Y., in the capacity of food and drug inspector, has recently resigned from that position to become research chemist in the laboratories of the Van Camp Packing Co., Indianapolis, Ind.

Mr. Henry N. Lyons, recently resigned his position as acid superintendent of the Kenvil Works, Hercules Powder Co., Kenvil, N. J., and has accepted the position of chief chemist for the Columbia Chemical Company, Barberton, Ohio.

GOVERNMENT PUBLICATIONS

By R. S. McBride, Bureau of Standards, Washington

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

CONGRESSIONAL COMMITTEES

Naval Stores. Hearings on S. 1351. 95 pp. This is for the purpose of establishing standard grades of naval stores.

Dyestuffs. Hearings on House Report 2706, to amend act to increase revenue and House Report 6495, to regulate importation of coal-tar products and to promote establishment of manufacture thereof in the United States. 739 pp.

Scientific Apparatus and Instruments. 35 pp. This was compiled by the Tariff Commission.

Cereal Beverages. Statement of Cleveland Newton in hearings of July 28, 1919. 7 pp.

Coal-Tar Products. House Report 209, submitted by Mr. Longworth to accompany House Report 8078, to regulate importation of coal-tar products and to promote establishment of manufacture thereof in the United States. 5 pp.

Dyes and Dyeing. Report on dyes and related coal-tar chemicals, 1918. Revised edition compiled by Tariff Commission. 103 pp.

Flour. Hearings on House Report 6814, to provide revenue and to promote production of potato flour and potato starch in the United States. 28 pp. Also: House Report 241, to accompany House Report 6814, submitted by Mr. Fordney to provide revenue and promote production of potato flour and potato starch in United States. 3 pp.

Fruit Juices. Unfermented fruit juices, hearings on House Report 7289 to provide revenue. 75 pp.

Lime. Statement of W. E. Humphrey in hearings of July 18, 1919. 14 pp.

Magnesite. Hearings on House Report 5218, to provide revenue and to establish production of magnesite ores and manufactures thereof in United States.

Potassium Salts. Hearings on House Report 4870, to provide revenue and to safeguard, by license control of imports of potassium salts and by imposing import duty thereon, interests of domestic potash producers.

Tariff. Statement of William Burgess in hearings of July 16, 1919, on anti-dumping and undervaluation. 16 pp.

Tungsten. Information concerning tungsten-bearing ores, including bibliography, compiled by Tariff Commission. 47 pp.

Tungsten. Hearings on House Report 4437 to provide revenue and promote production of tungsten ores. 5 pp.

Zinc. Duty on zinc ore. House Report 203 to accompany House Report 6238, submitted by Mr. Fordney. 2 pp. To provide revenue and establish production of zinc ores and manufactures thereof in United States.

HYGIENIC LABORATORY

Drugs. A. G. Dumez. Bulletin 118. 455 pp. Paper, 35 cents. Issued May 1919. This is a digest of comments on Pharmacopoeia of United States of America (8th decennial revision), and National Formulary (3rd edition).

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

Aluminum and Its Light Alloys. P. D. Merica. Report 34. 8 pp.

Testing of Balloon Fabrics. J. D. Edwards and I. L. Moore. Report 39. 18 pp. Includes two parts on: Characteristic exposure tests of balloon fabrics; and use of ultraviolet light for testing balloon fabrics.

Airplane Dopes and Doping. W. H. Smith. Report 38. 9 pp.

Fabric Fastenings. E. D. Walen and R. T. Fisher. Report 37. 14 pp.

Self-Luminous Material. N. E. Dorsey. Report 33. 16 pp.

Airplane Tensiometer. L. J. Larson. Report 32. 8 pp.

FEDERAL TRADE COMMISSION

Coal. Cost reports of Federal Trade Commission; No. 1 Pennsylvania bituminous. 103 pp.

Leather. 180 pp. Paper, 20 cents. A report on leather and shoe industries, 1914–1918. Issued August 1919.

Leather and Shoe Industries. 180 pp. House Document 196. Issued August 1919.

PUBLIC HEALTH SERVICE

A Study of the Munitions Intoxications in France. R. G. Perkins. Public Health Reports, **34**, 2335–75 (October 24).

Determination of Bacteritropic Content of Antimeningococcic Serum. A. C. Evans. Public Health Reports, **34**, 2375–78 (October 24).

Note on the Hygienic Laboratory Method of Standardizing Disinfectants. Public Health Reports, **34**, 2297 (October 17). "For the information of those employing the Hygienic Laboratory method of standardizing disinfectants, it seems desirable to call attention to a modification of that method which has been adopted at the Hygienic Laboratory."

Pollution of City Water Supply Enjoined. Public Health Reports, **34**, 2303 (October 17).

Laboratory Tests of Air-Measuring Bags and Disk-Valve Hand Pump for Mine Dust Sampling Apparatus. G. E. McElroy. Public Health Reports, **34**, 2434 (October 31).

WATERTOWN ARSENAL

Tests of Metals, Etc., for Industrial Purposes at Watertown Arsenal. House Document 242. 3 pp. Issued September 5, 1919.

GEOLOGICAL SURVEY

The Alaskan Mining Industry in 1918. G. C. Martin. Bulletin 712-A. Separate from Mineral Resources of Alaska, 1918-A. 52 pp.

This volume, like the others of the series, contains an account of the mining industry, including statistics of mineral production, and also preliminary statements on investigations made by the Geological Survey. It is intended that this series of reports shall serve as convenient reference works on the mining industry for the years which they cover. It is not possible for a member of the Survey to visit every mining district each year, and therefore the information used in preparing the summary on mining developments is in part obtained from other reliable sources.

The statistics for the mineral production of Alaska for the last two years are given in the following table. The minor metallic and nonmetallic products are grouped, because a separate listing might reveal the production of individual properties.

MINERAL OUTPUT OF ALASKA, 1917 AND 1918

	1917		1918		Decrease or increase in 1918	
	Quantity	Value	Quantity	Value	Quantity	Value
Copper, pounds	88,793,400	$24,240,596	69,224,951	$17,098,563	—19,568,449	—$7,142,033
Gold, fine ounces	709,050	14,657,353	458,641	9,480,952	— 250,409	— 5,176,401
Silver, fine ounces	1,239,150	1,021,055	847,789	847,789	— 391,361	— 173,266
Coal, short tons	53,955	265,317	75,606	411,850	+ 21,651	+ 146,533
Tin, metallic, short tons	100	123,300	68	118,000	— 32	— 5,300
Lead, short tons	852	146,584	564	80,088	— 288	— 66,496
Miscellaneous metallic products, including chrome ore, tungsten, antimony, platinum, and palladium	....	118,500[1]	....	96,100	....	— 22,400
Miscellaneous nonmetallic products, including petroleum, marble, gypsum, and lime	....	137,500[2]	....	120,619	....	— 16,881
	....	$40,710,205	....	$28,253,961	....	$12,456,244

[1] No palladium included.
[2] Some graphite included.

Peat in the Dismal Swamp of Virginia and North Carolina. C. C. OSBON. Bulletin 711-C. Contributions to Economic Geology, 1919, Part II. 19 pp. Published October 29, 1919.

Magnesite in 1918. C. G. YALE AND R. W. STONE. Separate from Mineral Resources of the United States, 1918, Part II. 18 pp. Published September 16, 1919.

The crude magnesite produced and sold or treated in the United States in 1918 amounted to 231,605 short tons, valued at $1,812,601, f. o. b. mines or plants. As compared with an output in 1917 of 316,838 tons, valued at $2,899,818, this was a decrease of about 27 per cent in quantity and 37 per cent in value. The reduction was not general, however, for while the California output fell from 211,663 tons in 1917 to 84,077 tons, a decrease of 60 per cent, the Washington output increased from 105,175 tons in 1917 to 147,528 tons, or 40 per cent.

According to the best data available, the average price per ton of crude magnesite f. o. b. mine in California fell from $10 in 1917 to about $9.06 in 1918, and in Washington from about $7.45 in 1917 to $7.12 in 1918.

MAGNESITE IMPORTED FOR CONSUMPTION IN THE UNITED STATES IN 1918

	Quantity (pounds)	Value
Magnesia:		
Calcined, medicinal	523	$ 312
Carbonate of, medicinal	....	.....
Sulfate of (epsom salts)	2,045	196
Magnesite:		
Calcined, not purified	38,098,815	824,022
Crude	10,864,000	103,233

Gold, Silver, Copper, and Lead in Alaska in 1918. G. C. MARTIN. Separate from Mineral Resources of the United States, 1918, Part I. 16 pp. Published October 30, 1919.

Gold, Silver, Copper, and Lead in South Dakota and Wyoming in 1918. C. W. HENDERSON. Separate from Mineral Resources of the United States, 1918. Part I. 10 pp. Published November 6, 1919.

Silver, Copper, Lead and Zinc in the Central States in 1918. J. P. DUNLOP AND B. S. BUTLER. Separate from Mineral Resources of the United States, 1918, Part I. 67 pp. Published October 31, 1919.

Gold, Silver, Copper, Lead, and Zinc in New Mexico and Texas in 1917. C. W. HENDERSON. Separate from Mineral Resources of the United States, 1917, Part I. 26 pp. Published November 8, 1919.

Mineral Resources of Seward Peninsula, Alaska. Bulletin 692-G. Separate from Mineral Resources of Alaska, 1917-G. This report includes the following three reports:

(1) **Tin Mining in Seward Peninsula.** G. L. HARRINGTON. 9 pp.

Lode mining in 1917 was confined to development work on Lost River and Ear Mountain without any production. Lost River is believed to have possibilities as a producer of lode tin. Further development is necessary at other properties.

Placer mining in 1917 was limited to the vicinity of Buck Creek. About 300 tons a year appears to be the limit of production for this area, and this production will be limited to a period of not over five years; after that time there will be production of only a few tons annually from sluicing operations. Placers may be developed in the vicinity of Ear Mountain, but the production in this vicinity will be small. On Lost River a few tons of residual placer tin may be recovered when water is available for sluicing. Anikovik River has a greater area of stream gravels which may be dredged than any of the other placers. A bedrock of finger slates, in a nearly vertical attitude and with numerous reefs, may interpose difficulties in dredging, involving a loss of some cassiterite and probably a considerable amount of the gold. The possibilities of the stream cannot be stated.

(2) **Graphite Mining in Seward Peninsula.** G. L. HARRINGTON. 5 pp. There appears to be an opportunity for the development of a large amount of graphite from these deposits. Transportation problems are relatively simple.

(3) **The Gold and Platinum Placers of the Kiwalik-Koyuk Region.** G. L. HARRINGTON. 30 pp.

Clays and Shales of Minnesota. F. F. GROUT. Bulletin 678. 259 pp. Paper, 25 cents. Work done in coöperation with the Minnesota Geological Survey.

This bulletin comprises a discussion of the distribution, origin, properties, classification, and adaptability of the clays and shales of Minnesota. An attempt has been made to test all the more important deposits with sufficient exactness to determine for what purposes they may be used. Detailed results of these tests are arranged by counties.

Preliminary Report on the Mineral Resources of the United States in 1918. Introduction by EDSON S. BASTIN; statistics assembled by M. B. CLARK, from data furnished by specialists of the Division of Mineral Resources. 106 pp. Issued August 7, 1919.

This pamphlet is the first of a new class of Survey reports which it is hoped will be of wide usefulness. Its purpose is to furnish to the public the statistics of mineral production in the United States within six months, if possible, after the end of the year covered by the statistics. For most commodities final figures are given; for a few only estimates based on incomplete returns can be given; but the data on the whole present a fairly complete picture of the progress of the mineral industry during the year. For final and more complete information readers are referred to the annual two-volume publication "Mineral Resources of the United States," which is usually issued between 13 and 18 mo. after the end of the year to which it refers. Although Mineral Resources cannot be published until the slowest chapter and the final summary chapter are printed most of the information which it contains is available much more promptly, for the chapter covering each commodity is issued as a pamphlet as soon as it is completed—some of them only 4 mo. after the end of the year.

Tin in 1918. A. KNOPF. Separate from Mineral Resources of the United States, 1918, Part I. 7 pp. Issued September 9, 1919.

The metallic tin obtainable from concentrate produced in the United States in 1918 amounted to 68 short tons. As in the past, practically all this concentrate was won from gravels mined in Alaska.

The tin imported in 1918 as metal and metal in concentrate reached the record quantity of 82,854 short tons, an increase of nearly 5,000 tons over imports in 1917. The metal imported and entered for consumption was 71,254 short tons and the tin produced by the domestic smelters, almost wholly from Bolivian concentrates, was 10,284 tons. The total supply of new or primary tin available for consumption was therefore 81,538 tons.

The world's output of tin in 1918 was about 144,000 short tons. The tin available for consumption in the United States therefore amounted to 57 per cent of the world's output.

The average price of spot Straits tin in New York in 1918 was 86.8 cents per lb., as compared with 61.65 cents for 1917.

The average price for the year in London was £329 11s. per ton of 2,240 lbs. The lowest price was £236 and the highest price was £399. The average price for 1918 was far above any previous record, but this increase in the price of tin over pre-war prices was relatively smaller than that of copper and other common industrial metals.

Salt, Bromine, and Calcium Chloride in 1918. R. W. Stone. Separate from Mineral Resources of the United States, 1918, Part II. 16 pp. Issued August 16, 1919.

The quantity of salt produced and sold in the United States in 1918 was 7,238,744 short tons, valued at $26,940,361, an increase of 3.7 per cent in quantity and 35.1 per cent in value over the production in 1917.

The figures show that the increase in the production of manufactured or evaporated salt in 1918 as compared with 1917 was 9.7 per cent and of rock salt 4.9 per cent. The production of brine salt decreased 2 per cent. The average price of all salt produced increased 30 per cent and was $3.72 a ton in 1918 as compared with $2.86 in 1917. This increase in price is a little less than the increase in 1917, which was 33 per cent, but was caused by the same things—higher wages and higher cost of fuel and other supplies.

Prices of Coal and Coke, 1913–1918. C. E. Lesher. Separate from Mineral Resources of the United States, 1918, Part II. 100 pp. Issued August 29, 1919. Prepared in coöperation with the United States Fuel Administration and War Industries Board.

Shorter Contributions to General Geology, 1918. D. White. Professional Paper 120. 206 pp. This includes nine short reports, the important ones of which have previously been separately reviewed.

Iron-Depositing Bacteria and Their Geologic Relations. E. C. Harder. Professional Paper 113. 89 pp.

"Mr. Harder concludes that, according to present knowledge, there are three principal groups of iron-depositing bacteria: (1) those that precipitate ferric hydroxide from solutions of ferrous bicarbonate, using the carbon dioxide set free and the available energy of the reaction for their life processes; (2) those that do not require ferrous bicarbonate for their vital processes but that cause the deposition of ferric hydroxide when either inorganic or organic iron salts are present; and (3) those that attack iron salts of organic acids, using the organic acid radical as food and leaving ferric hydroxide, or basic ferric salts that gradually change to ferric hydroxide.

"In addition to recording much that is new concerning iron-depositing bacteria, Mr. Harder's report constitutes a valuable critical summary of previous work and should serve a useful purpose in bringing before geologists a digest of practically all that is known on the subject, supplemented by a carefully prepared bibliography."

Phosphate Rock in 1918. R. W. Stone. Separate from Mineral Resources of the United States, 1918, Part II. 24 pp. Issued October 4, 1919.

The phosphate rock marketed in the United States in 1918 was 2,490,760 long tons, valued at $8,214,463. As compared with the production in 1917, which amounted to 2,584,287 long tons, valued at $7,771,084 there was a decrease in quantity of 93,527 tons, or 3.6 per cent, and an increase in value of $443,379, or 5.7 per cent. In this report the value of domestic material means selling value f. o. b. mines.

In 1918 there was a small increase in quantity of phosphate rock sold in Florida and South Carolina, but a larger decrease in quantity sold in Tennessee and the Western States, making a net decrease for the country. On the other hand, the average price per ton increased in all States, the percentages of increase being 9 in Florida, 7 in South Carolina, 24 in Tennessee, and 27 in the Western States. The increase in average price per ton in the whole country was from $3.01 in 1917 to $3.30 in 1918, or nearly 10 per cent.

Since 1913, when more than 1,300,000 tons of phosphate rock were exported, the quantity leaving the United States has steadily decreased until in 1918 it was only 143,455 tons, a little more than one-tenth of the exports of 1913. A table, compiled from reports of the Bureau of Foreign and Domestic Commerce, shows exports of phosphate rock in the last three years.

SMITHSONIAN INSTITUTION

Smithsonian Meteorological Tables. Based on Guyot's Meteorological and Physical Tables. 4th revised edition, corrected to January 1918. Publication 2493, Smithsonian Miscellaneous Collections.

TARIFF COMMISSION

Dyes and Dyeing. Tariff Information Series 11. 103 pp. This is a census of dyes and coal-tar chemicals for 1918.

BUREAU OF CENSUS

Stocks of Leaf Tobacco and American Production, Import, Export, and Consumption of Tobacco and Tobacco Products, 1918. Bulletin 139. 46 pp. Paper, 10 cents. Issued September 1919.

Report on stocks of leaf tobacco held semi-annually from October 1, 1912, to October 1, 1916, and quarterly since latter date. In addition to statistics of leaf tobacco held data are also shown regarding production, consumption, imports, and exports of tobacco, prices obtained for staple by growers, quantities of several products manufactured therefrom, and revenue on tobacco collected by United States Government.

BUREAU OF FISHERIES

Fresh-Water Mussels and Mussel Industries of United States. R. E. Coker. Bureau of Fisheries Document, 865. 79 pp. Paper, 40 cents.

BUREAU OF MINES

Production of Explosives in the United States during the Calendar Year 1918, with Notes on Coal-Mine Accidents Due to Explosives, and List of Permissible Explosives Tested Prior to March 31, 1919. A. H. Fay. Technical Paper 231. 21 pp. Paper, 5 cents. Issued August 1919.

The production for 1918 is segregated as follows: Black blasting powder, 246,663,350 lbs.; "high" explosives other than permissible explosives, 206,516,077 lbs.; and permissible explosives, 46,045,233 lbs. These figures represent a decrease of 30,455,175 lbs. of black powder, 55,800,003 lbs. of high explosives, and an increase of 3,004,511 lbs. of permissible explosives as compared with figures for 1917.

The decrease in the amount of black blasting powder used in coal mining was about 20,000,000 lbs.; this decrease was offset largely by an increase of about 3,000,000 lbs. of high explosives and 4,000,000 lbs. of permissible explosives. In metal mining there was a decrease in the amount of all classes of explosives used, largely because war conditions prevented the average amount of development work during the year and also because of the closing of many of the smaller mines, especially gold mines, and the general decrease in mining during the last two months of the year.

Abatement of Corrosion in Central Heating Systems. F. N. Speller. Technical Paper 236. 12 pp. Paper, 5 cents. Issued August 1919.

Sensitiveness of Explosives to Frictional Impact. S. P. Howell. Technical Paper 234. 17 pp. Paper, 5 cents. Issued September 1919.

Approximate Quantitative Microscopy of Pulverized Ores, Including the Use of the Camera Lucida. W. H. Coghill and J. P. Bonardi. Technical Paper 211. 17 pp. Paper, 5 cents. Issued October 1919.

An Analytical Method for Detecting Blown-Out Shots in Coal Mines. G. F. Hutchison and J. Barab. Technical Paper 210. 22 pp. Paper, 5 cents. Issued October 1919.

Why and How Coke Should Be Used for Domestic Heating. H. Kreisinger and A. C. Fieldner. Technical Paper 242. 20 pp. Paper, 5 cents. Issued October 1919.

BUREAU OF STANDARDS

Leakage Resistance of Street Railway Roadbeds and Its Relation to Electrolysis of Underground Structures. E. R. Shepard. Technologic Paper 127. 39 pp. Paper, 10 cents. Issued October 6, 1919.

Tests of Flexible Gas Tubing. R. S. McBride and W. M. Berry. Technologic Paper 133. 37 pp. Paper, 10 cents. Issued October 27, 1919.

Standardization of the Sulfur Boiling Point. E. F. Mueller and H. A. Burgess. Scientific Paper 339. 22 pp. Paper, 5 cents. Issued October 4, 1919. It is the purpose of this paper to present further evidence on the effect of these experimental conditions with the object of making this evidence sufficiently complete to serve as a basis for standard specifications for the use of the sulfur boiling point as a calibration temperature. The work was therefore planned so as to supplement and complete, in so far as possible, the work of previous investigators.

Measurements of Wave Lengths in the Spectra of Krypton and Xenon. P. W. Merrill. Scientific Paper 345. 7 pp. Paper, 5 cents. Issued October 3, 1919.

This paper records photographic measurements of wave lengths in the spectra of krypton and xenon, principally in the red and infra-red. In krypton 37 new lines were measured between 6576 Å and 8928 Å; in xenon 52 new lines between 6318 Å and 9162 Å. In this region there are numerous strong lines which are probably among the most important in the spectra of these elements. The xenon lines at 8231 Å and 8280 Å are especially notable. These and other lines may be of value as wave-length standards in the infra-red. Attention is called to a probable analogy between the spectra of the rare gases neon, argon, krypton, and xenon which this investigation has brought to light.

Use of a Modified Rosenhain Furnace for Thermal Analysis. H. Scott and J. R. Freeman, Jr. Scientific Paper 348. 7 pp. Paper, 5 cents. Issued October 24, 1919.

A description is given of a thermal-analysis furnace constructed on the principle of Rosenhain's furnace, the chief departures from his design being: (1) Use of a gravity-drive rate control, and (2) introduction of the sample through the bottom and cold end of the furnace. The advantages and faults of these modifications are mentioned. The methods of operation developed and adopted for use with this furnace are described and discussed, the principal variation from the usual practice being the mounting of the sample in direct thermal contact with the thermocouple.

Photoelectric Spectrophotometry by the Null Method. K. S. Gibson. Scientific Paper 349. 28 pp. Paper, 5 cents. Issued October 11, 1919.

Application of the Interferometer to Gas Analysis. J. D. Edwards. Technologic Paper 131. 19 pp. Paper, 5 cents. Issued October 6, 1919. The principle of the gas interferometer and its method of use in gas analysis is discussed in connection with the calibration of the instrument. The effect produced upon the observations by variations in gas composition and experimental conditions is analyzed and equations developed by which the magnitude of such changes can be estimated. Typical cases in which the interferometer may be employed, such as for the analysis of mixtures containing helium, analysis of flue gas, etc., are given, together with points on sources of error, details of operation, and the relative sensitivity of the interferometer for different gases.

Mechanical Properties and Resistance to Corrosion of Rolled Light Alloys of Aluminum and Magnesium with Copper, with Nickel, and with Manganese. P. D. Merica, R. G. Waltenberg and A. N. Finn. Technologic Paper 132. 13 pp. Paper, 5 cents. Issued October 25, 1919.

Light aluminum alloys of several compositions belonging to each of the three ternary series, aluminum-magnesium-copper, aluminum-magnesium-manganese, and aluminum-magnesium-nickel, were rolled out into sheet and tested in tension as cold-rolled, after annealing, and after heat treatment, consisting of quenching from about 500° C. and ageing at ordinary temperature.

The alloys of the aluminum-magnesium-copper series were superior in all conditions to those of the other series in respect to tensile properties. The tensile properties of the aluminum-magnesium-copper series may be much improved by an appropriate heat treatment. The alloys of the aluminum-magnesium-nickel series are also improved by heat treatment, but not in the same degree as the former series. The alloys of the aluminum-magnesium-manganese series are not improved by heat treatment.

Samples of representative compositions of each series were exposed to corrosion in the salt-spray test, and the appearance of the samples observed after one and after two months' exposure to the action of the salt spray. The alloys of the aluminum-magnesium-manganese series resisted corrosion in general better than those of the other series, and this agrees with other experience in the corrosion of such alloys. The heat-treated specimens of the aluminum-magnesium-copper series were, however, but little inferior to those of the manganese series in their resistance to corrosion; the annealed and the cold-rolled samples of that series were the least resistant to corrosion of any of the alloys tested. Hard-rolled commercial aluminums corroded much more than any of the alloys. Annealed aluminum was more resistant to corrosion than the hard-rolled aluminum, but did not compare favorably with most of the alloys.

Behavior of Wrought Manganese Bronze Exposed to Corrosion while under Tensile Stress. P. D. Merica and R. W. Woodward. Technologic Paper 135. 9 pp. Paper, 5 cents. Issued October 16, 1919.

Effects of Glucose and Salts on the Wearing Quality of Sole Leather. P. L. Wormeley, R. C. Bowker, R. W. Hart and L. M. Whitmore, in coöperation with J. B. Churchill, Director American Leather Research Laboratory. Technologic Paper 138. 38 pp. Paper, 10 cents. Issued October 6, 1919.

Some Tests of Light Aluminum Casting Alloys—The Effect of Heat Treatment. P. D. Merica and C. P. Karr. Technologic Paper 139. 31 pp. Paper, 10 cents. Issued October 24, 1919.

The tensile properties and the hardness of a number of different compositions of light aluminum casting alloys have been determined; the resistance to corrosion compared and the resistance to the action of alternating or vibratory stresses determined of a few commonly used compositions.

Constant-Temperature Still Head for Light-Oil Fractionation. F. M. WASHBURN. Technologic Paper 140. 12 pp. Paper, 5 cents. Issued October 18, 1919.

The three types of methods generally in use for the fractionation of light oil and the determination of benzene, toluene, and solvent naphtha are discussed. An apparatus which is an improvement on the dephlegmator of the Wilson and Roberts still is described, and the details of its operation are given. The apparatus is easily and inexpensively constructed and requires no greater attention or time than others used. Exceptionally large volumes of "pure" fractions are obtained which have a very small boiling-point range, showing that they contain only negligible amounts of impurities. Almost all of each of the components of the mixture distilled is obtained in practically the pure state since the volumes of each of the intermediate fractions are only about 1.5 per cent of the volume taken for distillation. The composition of each of the intermediate fractions is actually determined, and the error introduced by this determination is small, since it is applied to only small volumes. The apparatus works well on mixtures containing widely varying percentages of benzene, toluene, and solvent naphtha.

Direct Determination of India Rubber by the Nitrosite Method. J. B. TUTTLE AND L. YUROW. Technologic Paper 145. 16 pp. Paper, 5 cents. Issued October 22, 1919.

Harries and his co-workers claimed that there is no loss of carbon when the rubber molecule passes through the process for the formation of the nitrosite. Wesson's combustion method for the direct determination of rubber depends upon the correctness of this claim. An examination of his method shows that, although he obtained fairly satisfactory results, there are certain avoidable sources of error. Compounds containing new rubber and no substitutes or organic fillers can be analyzed with correct results, owing to a balancing of errors. By suitable changes in the procedure of Wesson the present authors have succeeded in obtaining very satisfactory results, not only with pure gum compounds, but also with compounds made up with reclaimed rubber, mineral rubber, oil substitutes, lampblack, etc.

Protective Metallic Coatings for the Rustproofing of Iron and Steel. Circular 80. 34 pp. Paper, 10 cents. Issued October 4, 1919.

Household Weights and Measures. Miscellaneous Publications 39. This is a card, the object of which is to present in convenient form the tables of weights and measures most useful for household purposes.

DEPARTMENT OF AGRICULTURE

The Production and Conservation of Fats and Oils in the United States. H. S. BAILEY AND B. E. REUTER. Supplement to Department Bulletin 769. 7 pp. Paper, 5 cents. Issued October 29, 1919. This publication completes the report of the fats and oils survey conducted by the Government during 1917 and 1918.

Use of Toxic Gases as a Possible Means of Control of the Peach-Tree Borer. E. E. BLAKESLEE. Department Bulletin 796. 23 pp. Paper, 5 cents. Issued October 21, 1919.

A Survey of the Fertilizer Industry. E. A. GOLDENWEISER. Department Bulletin 798. 29 pp. Paper, 10 cents. Issued October 20, 1919. This is a report upon the production and disposal of fertilizing materials during 1917 and 1918.

The Mosaic Disease of Sugar Cane and other Grasses. E. W. BRANDES. Department Bulletin 829. 26 pp. Paper, 10 cents. Issued October 20, 1919.

COMMERCE REPORTS—OCTOBER 1919

The regulations for the importation into the United States of German vat dyes through the Textile Alliance are published. (P. 253)

The Central Union of Russian Coöperative Societies (*Centrosoyuz*) conducts a chemical **laboratory for testing** goods made or purchased by the various coöperative organizations. A chemical factory is also maintained for the manufacture of **extracts, essences, oils,** etc., and also several plants for the manufacture of **molasses, starch,** etc. (Pp. 314–8)

A process has been devised in Australia for the manufacture of **textiles** such as twine, rope and bagging from the bark of the eucalyptus tree. (P. 361)

Bismuth obtained as a by-product from tungsten ore is being shipped from China to the United States and Great Britain. (P. 379)

Under the direction of the Indian Munitions Board there has been a great development of the **tanning industry** in India. (Pp. 388–94)

Extensive deposits of **iron and manganese ores** have been discovered near Coblenz, Germany. (P. 526)

Among the **chemical industries** of Turkey are sulfuric and nitric acids, lead smelting, lime, cement, ceramics, glass, illuminating gas, carbon dioxide, oxygen, olive oil, cottonseed oil, essential oils, soap, licorice, tanning and dyeing. (Pp. 545–51)

The **Chilean nitrate** situation is rapidly becoming normal and both production and shipment are increasing. (P. 635)

SPECIAL SUPPLEMENTS ISSUED IN OCTOBER

NETHERLANDS—9*b*
SPAIN—15*d* and 3
SWITZERLAND—17*a*
WALES—19*d*
UNITED KINGDOM—19*c*
PANAMA—35*a*
PARAGUAY—45*a*
CHINA—52*c* and *d*
NEW ZEALAND—61*a*

STATISTICS OF EXPORTS TO THE UNITED STATES

HONGKONG—
(P. 276)
Antimony
Chemicals
Earthenware
Hides
Peanut oil
Wood oil
Cassia oil
Manganese ore
Tungsten ore
Paper
Sugar
Tin

CHINA—
Sup. 52*c* and 52*d*
Antimony
Albumen
Camphor
Gall nuts
Musk
Rhubarb
Copper
Fibers
Grease
Hides
Bean oil
Castor oil
Cottonseed oil
Peanut oil
Rape oil
Sesame oil
Wood oil
Tungsten ore
Platinum
Paraffin

WALES—Sup. 19*d*
Abrasives
Nickel sulfate
Nickel ammonium sulfate
Oxalic acid
Copper matte
Hides

LONDON—Sup. 19*c*
Abrasives
Asbestos
Bismuth
Brass
Celluloid
Chemicals
Drugs
Fullers' earth
Copper matte
Creosote oil
Fertilizers
Glassware
Galalith
Glue
Grease
Gums
Hides
Rubber
Indigo
Iridium
Mica
Paper stock
Picture films
Platinum
Graphite
Soap
Tin
Wax

NETHERLANDS—
Sup. 9*b*
Balances
Chemicals
Drugs
Dyes
Cocoa butter
Decolorizing carbon
Diamonds
Chinaware
Fertilizers
Fibers
Hides
Glassware
Glue
Matches
Paints
Paper
Sugar beet seeds

SWITZERLAND—
Sup. 7*a*
Drugs
Aniline colors
Artificial indigo
Synthetic perfumes

PANAMA—Sup 35*a*
Rubber
Copra
Hides
Ipecac
Manganese ore
Tagua
Tallow
Cottonseed
Fustic

COMMERCE REPORTS—NOVEMBER 1919

The production of **glycerin** in the United States has increased to such an extent that imports of 20,000,000 to 40,000,000 pounds annually before 1914 have decreased to about 1,000,000 pounds in 1919. Exports have increased to 21,000,000 pounds in 1918. (Pp. 796–801)

Statistics are given regarding the United States production, consumption and present stocks of various **vegetable, fish and animal oils.** (Pp. 927–929)

The resumption of **zinc smelting** in Belgium has been hampered by the difficulty of importing ore from Australia and other former sources of supply. (P. 935)

The discovery of **petroleum** in large amount is reported from Papua (British New Guinea). (P. 1000)

Belgian **window-glass** plants are all in operation as are most of the plate glass plants. Production is still below normal, owing to lack of raw materials. (P. 1048)

Statistics of the production of **platinum** in Russia include the average composition of the crude platinum from the three principal deposits in the Urals. It is estimated that a troy pound of platinum costs the Omsk government about $732. (Pp. 1095–7)

The **metric system** has been adopted exclusively in Poland and the use of other measures is prohibited by law. (P. 1135)

In a report on the German potash situation it is stated that the present production of the Kali Syndicate is only about 85 per cent of the output in 1917, due to **coal** shortage. (Pp. 1185–7)

A new **copper smelter** is to be erected at Oroya, Peru, with a daily capacity of 2500 tons of ore. It will employ a staff of 200 to 300 Americans and 3000 to 4000 native workmen. (P. 1197)

A detailed description of the **mineral resources** of the Caucasus includes data on petroleum and ores of manganese, copper, silver, lead, zinc, cobalt, nickel, antimony, sulfur, pumice, and coal. (Sup. 13*a*)

SPECIAL SUPPLEMENTS ISSUED IN NOVEMBER

GREECE—7*a*
ITALY—8*b*
PORTUGAL—11*a*
RUSSIA (Caucasus)—13*a*
ECUADOR—43*a*
CHINA—52*e* and *f*
BRITISH SO. AFRICA—66*b*
CEYLON—51*a*
MEXICO—32*b* and *c*

STATISTICS OF EXPORTS TO THE UNITED STATES

SWATOW, CHINA—(P. 1162)
Alum
Jute
Peanuts
Indigo
Tungsten ore
Peanut oil
Paper
Sugar

MEXICO—Sup. 32*b* and 32*c*
Chicle
Copra
Hides
Logwood
Rubber
Calcium citrate
Copper
Lead
Manganese ore
Mercury
Tin ore
Beeswax
Candelilla wax
Tungsten ore
Fustic
Glycerin

GREECE—Sup. 7*a*
Gum mastic
Herbs
Licorice
Olive oil
Opium
Hides

PORTUGAL—Sup. 11*a*
Antimony
Argols
Ergot
Rubber
Palm oil
Salt
Tungsten ore

ECUADOR—Sup. 43*a*
Annatto
Cinchona bark
Gold
Ivory nuts
Kapok
Hides
Leather
Manganese ore
Rubber
Zinc

CEYLON—Sup 51*a*
Cinnamon oil
Citronella oil
Coconut oil
Copra
Fiber
Graphite
Rubber

HONGKONG, CHINA—Sup. 52*e*
Tungsten ore
Tin
Antimony
Essential oils
Vegetable oils
Peanuts

BRITISH SO. AFRICA—Sup. 66*b*
Asbestos
Copper
Diamonds
Chrome ore
Corundum
Manganese ore
Hides
Wax

BOOK REVIEWS

The Chemists' Year Book, 1918–1919. Edited by F. W. ATACK, M.Sc. Tech. (Manch.), B.Sc. (London), Fellow of the Institute of Chemistry. Assisted by L. WHINYATES, Assoc. M.S.T. 2 vols., 1146 pp. London: Sherratt & Hughes, 1919. Price, post-free, 15s. 6d.; foreign, 16s.

In this, the fourth edition of The Chemists' Year Book, the table of properties of inorganic compounds has been enlarged by thirty-two and that of organic compounds by thirty pages. There are new sections on the "Analysis of Clays, Firebricks and Silica Materials;" "Agricultural Chemistry;" and "Crystallography." The sections on "Dairy Products," "Electrochemistry," "Water Analysis," "Tannin Materials," and "Alkaloids," and the tables of the "Properties of the Essential Oils" have all been revised. Great care has apparently been taken to maintain a high standard of workmanship throughout the book. It is a satisfaction to have at hand a reference book in English of this character and completeness. This edition may well find a place in every library and laboratory.

H. P. TALBOT

The Second Report on Colloidal Chemistry and Its General and Industrial Applications, 1918. 172 pp. Price, 1s. 6d.

This report is the outcome of the work during 1918 of a committee appointed by the Chemical Section of the British Association for the Advancement of Science. On account of financial difficulties it was published by H. M. Stationery Office on behalf of the Department of Scientific and Industrial Research.

This valuable book contains reports by such men as Bancroft, Hatschek, Briggs, Harrison, Russell, Arden, Clayton, Bayliss, Searles, on peptization, emulsions, banding, electrical endosmose, the colloid features of textiles, the colloid chemistry of agriculture, sewage treatment, colloid problems of the dairy industry, physiology, and the treatment of disease.

Remarkably full lists of references are given, and stress is laid on the commercial applications of colloid chemistry.

Such reports are a great aid to research workers and should be expanded into longer monographs. It is to be hoped that this publication will be supplemented and revised every two or three years.

HARRY N. HOLMES

Catalysis in Industrial Chemistry. By G. G. HENDERSON. Monographs on Industrial Chemistry, edited by THORPE. 202 pp. Longmans, Green & Co., New York City, 1919. Price, $3.00.

The ideal monograph would be such a balanced and critical presentation of the subject matter that the reader would not need to refer to earlier papers except for minor details. Such a presentation, however, is possible only in so far as the author has first-hand information and experience of the subject, which in turn implies that the scope of the monograph should not be too broad. In the present instance, in which applications of catalytic processes to manufacturing operations of the most diverse character are treated, it is hardly possible that the author could have first-hand knowledge of more than a small proportion of the several applications, particularly so in view of the usual endeavor to keep such processes secret. Consequently the treatment is quite uneven, and in many cases consists of little more than a paraphrase of patent claims, which in such cases cannot always be regarded as giving reliable information. On the other hand, his discussion of certain processes, such as the contact process for sulfuric acid, appears to be satisfactory, although in this case one would have liked to see a more thorough treatment of the equilibrium involved than that given, which is as follows: "In the reaction between sulfur dioxide and oxygen of course the law of mass action holds, so that the complete conversion of the sulfur dioxide into sulfuric anhydride is impossible with the reacting gases mixed in the exact theoretical proportion; this can only be effected by having an excess of oxygen present. If chamber gases are used (containing, say, 7 volumes of sulfur dioxide, 10 volumes of oxygen, and 83 volumes of nitrogen) the nitrogen is without influence except that it affects the velocity of the reaction. The limit of the reaction is dependent solely upon the temperature, and not upon the nature of the catalyst. At temperatures below 200° there is no reaction, while at 900° to 1000° sulfuric anhydride is dissociated into sulfur dioxide and oxygen; between these limits the reaction occurs, reaching a maximum at about 450°. Hence in order to increase the velocity of the reaction as much as possible a catalyst which has its greatest activity at about 450°

should be used; the catalyst which best fulfils this condition is platinum." Wherever possible it would be advisable to include quantitative statements as to the equilibrium relations under various conditions of temperature and composition, because such data enable one to ascertain much more readily the best conditions for carrying out the process; for catalytic agents merely increase the rate of reaction but do not in general affect the real equilibrium, and so one wishes to secure conditions such that the equilibrium of the system is as favorable as possible, consistent with a rate of reaction great enough to be economically feasible.

The book contains much information that will be new to most readers; curiously enough, there is no mention of the applications of radiant energy as a catalyst. It includes a list of the principal catalysts of which applications are illustrated, and a subject index. The references to patents are unsatisfactory, in that neither the name of the patentee nor the year of issue is in general given, omissions which increase greatly the labor of looking up the original description of the process.

JOHN JOHNSTON

Condensed Chemical Dictionary. Compiled and edited by the staff of the Chemical Engineering Catalog, F. M. TURNER, JR., Technical Editor; D. D. BEROLZHEIMER, W. P. CUTTER, JOHN HELFRICH, Assistant Editors. 525 pp. The Chemical Catalog Co., Inc., 1 Madison Ave., New York. Price, buckram, $5.00; flexible cover with thumb index, $6.00.

Here is a book which will be hailed with joy by the layman who has to deal with commercial chemicals, and which will prove useful to the chemist as well. It is not a brief general dictionary of chemical terms, as the title would suggest, but a dictionary of the more important chemicals together with drugs, minerals and other substances. "A Condensed Dictionary of Chemicals" would have been a better name.

A typical definition will give the best idea of the book (the asterisk means "made in America"):

> **Ethyl Acetate.*** (Acetic ether; Vinegar naphtha) $CH_3CO_2C_2H_5$.
> Color and properties: Colorless, fragrant, inflammable liquid.
> Constants: Specific gravity 0.9003; melting-point —82.4° C.; boiling point 77.15° C.
> Soluble in water, alcohol and ether.
> Derivation: By heating acetic acid and ethyl alcohol in presence of sulfuric acid.
> Methods of purification: Rectification.
> Grades: Technical; U. S. P.; B. P.
> Containers: Iron drums.
> Uses: Medicine, solvent, organic synthesis, flavoring, perfumery.
> Fire hazard: Dangerous.
> Railroad shipping regulations: Red label.

A careful count indicates that there are approximately 6,000 entries, but as more than half of these are cross references the number of substances defined is probably about 2,500. Some selected entries show the field covered: acid alpha-naphthylamine sulfonic, acid iodic, allspice oil, apatite, asbestos, bakelite, Blau gas, Huber's reagent, salol, trinitrotoluene. Important trade and proprietary names have been included for the good reason that they are often not recognized in the trade as such; names of dyestuffs which might not be recognized as such are also entered. Adamsite, lewisite and other substances which have recently found use in warfare are briefly mentioned, but not the new explosives, such as anilite. The dictionary proper is followed by 18 pages of tables of atomic weights, and of weights and measures, conversion tables for specific gravity and temperature, and shipping regulations.

The full system of cross-indexing is a valuable feature of the book, one that is too often neglected.

The authors are to be commended for following the spelling rules of the AMERICAN CHEMICAL SOCIETY as used in *Chemical Abstracts*, and the reviewer, as a member of the SOCIETY'S committee on spelling, nomenclature and pronunciation, wishes to express his appreciation of this. Writers on technical chemistry, as a rule, pay little attention to spelling standards. Of course established usage in the spelling of commercial terms must be taken into account, and this the compilers have done, but uniformity between trade terms and scientific names is an ideal to be striven for. In this matter a dictionary can either help or hinder greatly.

As to the execution of the work, the reviewer regrets to say it leaves a good bit to be desired. Space has been unnecessarily wasted. To say nothing of the repetition of such long phrases as "methods of purification" and "railroad shipping regulations" in every definition, in several cases the same substance has been defined more than once under different names, *e. g.*, cananga oil and ylang-ylang oil; ethyl carbamate and urethane; stearin and tristearin; copal, gum animi and gum kauri (synonymous in part); carborundum, crystolon, and electrolon. In the latter case, if it was not desired to give preference to any one trade name the definition could have been put under silicon carbide and cross references made. Also, it is interesting to find a list of the States of the Union under "Cement rock" but would it not have been simpler to give the five in which cement rock is *not* found?

The cross references have not been carefully checked. Several direct the reader to nonexistent entries, as: "Dioxytoluene, see Orcin," and "Acetaminosalol, see Salophen." On the other hand important ones are omitted, as: "Acid arsenic, see Acid ortho-arsenic," and "Levulose, see Fructose."

Representation of ring formulas on one line is not always happy; for instance, diazobenzenesulfonic acid, $C_6H_4NSO_3N$, and quinoline, $(CH.CH)_2C_2CHCHNCH$. The empirical formulas would have been better.

In spite of the attempt to conform to the SOCIETY spellings, there are numerous entries which have some other spelling with no cross reference given (*e. g.*, acetine, cholesterin, dextrine, pyrrol, thermit, tolidin). The word "ester" has been wrongly used under the entries safrol, anethol, guaiacol, etc.; these compounds are ethers. The use of hydroxy *vs.* oxy and of amino *vs.* amido is not consistent.

It would be hardly fair to call attention to omissions in a condensed dictionary, but considering the things that are included one might fairly expect to find chicle, nitrogen peroxide, lard, novocaine, salophen, stovaine and other substances that are found in trade lists of drugs and chemicals. As a rule, however, important substances are included.

But the most serious criticism is upon the physical constants. The writer has made no attempt to check these systematically, but the trials that were made are discouraging. Titanium tetrachloride is described as a colorless liquid melting at 820° and having a specific gravity of 4.59. In reality it melts at —25° and has a specific gravity of 1.720 at 20°. Silicon tetrachloride is made to boil at 59.6° instead of 56.9°. This, of course, might be one of the typographical errors which are rather frequent, but there is no excuse for giving hydrocyanic acid the boiling point of *hydrochloric acid* (—83.1° instead of 25.2°) or hydrofluoric acid the melting point of *hydriodic acid* (—51.3° instead of —92.3°). Such occurrences, of course, destroy all confidence in the accuracy of the constants. Accordingly it is rather superfluous to point out that the value of 1.19867 for the specific gravity of nitrobenzene looks lonesome without its temperature. Yet this is the usual thing, the omitted temperatures varying from 0° to 25° or higher.

Apparently, the chief usefulness of the book will lie in identifying substances and in giving their uses and commercial grades. The latter are described very fully in some instances, *e. g.*, peanut oil.

The book is well printed and very attractively bound. Wide spacing and wide margins have been purposely provided for notes.

AUSTIN M. PATTERSON

NEW PUBLICATIONS

By Clara M. Guppy, Librarian Mellon Institute of Industrial Research, Pittsburgh

Alkali Industry. J. R. Partington. 8vo. 304 pp. Price, $3.00. D. Van Nostrand Co., New York.

Babbitt: Analysis of Babbitt. James Brakes. 169 pp. Price, $2.00. Allen Book and Printing Co., 454 Fulton St., New York.

Chemical Analysis: Textbook of Quantitative Chemical Analysis. A. C. Cummings and S. A. Kay. 3rd Ed. 416 pp. Gurney and Jackson, London.

Chemistry: Exercises in Chemistry. W. A. Noyes and B S. Hopkins. 12mo. 131 pp. Price, $0.80. Henry Holt & Co., New York.

Chemistry: Profession of Chemistry. R. B. Pilcher. 8vo. 213 pp. Price, 6s. 6d. Constable & Co., Ltd., London.

Chiropractic Chemistry: Textbook on Chiropractic Chemistry. S. J. Burich. 8vo. 430 pp. Price, $5.00. S. J. Burich, Davenport, Ia.

Dyeing: A Manual of Dyeing. Edmund Knecht, Christopher Rawson and Richard Loewenthal. 2 Vol. 5th Ed. 8vo. 383 pp. Price, 42s. per set. Charles Griffin & Co., London.

Dyeing: Modern Dyeing Methods; The Application of the Coal-Tar Dyestuffs; the Principles Involved and the Methods Employed. C. M. Whittaker. 8vo. 214 pp. Price, $3.00. D. Van Nostrand Co., New York.

Electrical Engineering Papers. B. G. Lamme. 773 pp. Price, $2.50. The *Electric Journal*, 1204 Keenan Building, Pittsburgh, Pa.

Electro- and Physical Chemistry: Quantitative Analysis by Electrolysis. Alexander Classen and H Cloeren. Revised English Translation of the Fifth German Edition. 346 pp. Price, $3.00. John Wiley & Sons., Inc., New York.

Electrochemical Industry: A Reference List of the Electrochemical Industry. American Electrochemical Society. 8vo. 52 pp. Price, $1.00. American Electrochemical Society, Bethlehem, Pa.

Forest Products: Their Manufacture and Use. N. C. Brown. 8vo. 471 pp. Price, $3.75. John Wiley & Sons., Inc., New York.

Iron and Steel: A Treatise on the Smelting, Refining and Mechanical Processes of the Iron and Steel Industry. E. V. Oberg and F. D. Jones. 8vo 328 pp. Price, $2.50. Industrial Press, New York.

Iron Bacteria. David Ellis. 8vo. 200 pp. Price, 10s. 6d. Methuen & Co., Ltd., London.

Manufacture of Chemicals by Electrolysis. A. J. Hale. 8vo. 80 pp. Price, 6s. Constable & Co., Ltd , London.

Perfumes and Cosmetics: Their Preparation and Manufacture. G. W. Askinson. Revised Ed. 334 pp. Price, 25s. Hodder & Stoughton, London.

Receipts: Techno-Chemical Receipt Book, Containing Several Thousand Receipts and Processes. W. T. Brannt and W. H. Wahl. New Enlarged Edition. 12mo. 516 pp Price, $2.50. H. C. Baird & Co., New York.

Rubber: Crude Rubber and Compounding Ingredients. H. C. Pearson. 3rd Ed. 8vo. 422 pp. Price, $10.00. The India Rubber World, New York.

Sewage Disposal. L. P. Kinnicutt, C. E. A. Winslow and R. W. Pratt. 2nd Ed. Rewritten. 547 pp. Price, $4.00. John Wiley & Sons, Inc., New York.

Scientific Discovery: Wonders of Scientific Discovery. C. R. Gibson. 8vo. 158 pp. Price, 3s. Seeley, Service & Co., Ltd., London.

Scientific Management: Two Papers on Scientific Management, A Piece-Rate System, and Notes on Belting. F. W. Taylor. 8vo. 230 pp. Price, 5s. G. Routledge & Sons, London.

Stereo-Chemistry. A. W. Stewart. 2nd Ed. 277 pp. Price, 12s. 6d. Longmans, Green & Co., London.

Tomato Products. Manufacture of, Including Whole Tomato Pulp or Puree, Tomato Catsup, Chili Sauce, Tomato Soup, Trimming Pulp. W. G. Hier. 12mo. 132 pp. Price, $5.00. W. G. Hier, Denver, Colo.

Zinc: A Bibliography on the Roasting, Leaching, Smelting and Electrometallurgy of Zinc. H. L. Wheeler. 8vo. 388 pp. University of Missouri School of Mines and Metallurgy, Rolla, Mo.

NEW JOURNAL

Giornale di Chemica Industriale. A Journal Established by the Coöperation of Italian Industrial Societies. Will correspond in Italian to the French *Chimie et Industrie*. Published monthly at 10, Via San Paolo, Milan. Price, 40 lire.

RECENT JOURNAL ARTICLES

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Aluminum Welding: The Chill in Aluminum Welding. David Baxter. *Acetylene Journal*, Vol. 21 (1919), No. 5, pp. 336, 338–341, 350.

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Leather: Dyeing and Tanning of Leather. Article II. John Helfrich. *Color Trade Journal*, Vol. 5 (1919), No. 5, pp. 134–137.

Magnesite in Building Construction. The General Application of Magnesia Cements to Exterior and Interior Works. W. C. Phalen. *Canadian Chemical Journal*, Vol. 3 (1919), No. 12, pp. 404–407.

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Tannin: Effect of Hard Water on Tannin. Report of 1919 Committee. T. A. Faust. *Journal of the American Leather Chemists' Association*, Vol. 14 (1919), No. 9, pp. 505–506.

Tanning: The Chrome Tanning Industry in Great Britain. M. C. Lamb. *Journal of the American Leather Chemists' Association*, Vol. 14 (1919), No. 11, pp 605–613.

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Tanning and Finishing Sheep Skins; English Methods; Colored Work-Acids Used. F. T. Howard. *The Leather Manufacturer*, Vol. 30 (1919), No. 10, pp. 335–337.

Transformer Tank: New Form of Tank for Static Transformers. W. S. Moody. *General Electric Review*, Vol. 22 (1919), No. 10, pp. 756–759.

Uranium: The Electrochemistry of Uranium and the Single Potentials of Some Oxides of Uranium. C. A. Pierlé. *Journal of Physical Chemistry*, Vol. 23 (1919), No. 8, pp. 517–553.

Vapor Pressure: Improved Apparatus for the Estimation of Vapor Pressures. Allan Morton. *Journal of the Society of Chemical Industry*, Vol. 38 (1919), No. 19, pp. 363*t*–364*t*.

MARKET REPORT—DECEMBER, 1919

WHOLESALE PRICES PREVAILING IN THE NEW YORK MARKET ON DECEMBER 15, 1919

INORGANIC CHEMICALS

Acetate of Lime, Basis 80%	100 Lbs.	2 00	@	2.05
Alum, ammonia, lump	100 Lbs.	4.25	@	4.50
Aluminum Sulfate (iron-free)	Lb.	$3\frac{1}{2}$	@	$3\frac{3}{4}$
Ammonium Carbonate, powdered	Lb.	13	@	$13\frac{1}{2}$
Ammonium Chloride, granular	Lb.	13	@	14
Aqua Ammonia, 25°	Lb.	$8\frac{3}{4}$	@	9
Arsenic, white	Lb.	$10\frac{1}{2}$	@	11
Barium Chloride	Ton	85.00		
Barium Nitrate	Lb.	11	@	13
Barytes, prime white		nominal		
Bleaching Powder, 35 per cent, Works	100 Lbs.	2.40	@	2.50
Blue Vitriol	Lb.	$8\frac{1}{8}$	@	$8\frac{1}{4}$
Borax, crystals, in bags	Lb.	$8\frac{1}{2}$	@	$8\frac{3}{4}$
Boric Acid, crystals	Lb.	$14\frac{1}{4}$	@	$14\frac{1}{2}$
Brimstone, crude	Long Ton	45.00	@	50.00
Bromine, technical, bulk	Lb.	55	@	1.00
Calcium Chloride, lump, 70 to 75% fused	Ton	20.00	@	25.00
Caustic Soda, 76 per cent	100 Lbs.	3.80	@	3.85
Chalk, precipitated	Lb.	$4\frac{1}{2}$	@	9
China Clay, imported	Ton	18.00	@	23.50
Feldspar	Ton	8.00	@	15.00
Fullers' Earth	100 Lbs.	1.50	@	2.00
Glauber's Salt	100 Lbs.	1.50	@	1.60
Green Vitriol, bulk		nominal		
Hydrochloric Acid, commercial, 22%	100 Lbs.	2.50	@	3.00
Iodine, resublimed	Lb.	4.25	@	4.30
Lead Acetate, white crystals	Lb.	$13\frac{1}{2}$		
Lead Nitrate	Lb.	15		
Litharge, American	Lb.	11	@	13
Lithium Carbonate	Lb.	1.50		
Magnesium Carbonate, powdered		13		15
Magnesite, "Calcined"	Ton	70.00	@	75.00
Nitric Acid, 40°	Lb.	6.75	@	7.25
Nitric Acid, 42°	Lb.	7.00	@	7.50
Phosphoric Acid, 48/50%	Lb.	$21\frac{1}{2}$	@	$23\frac{1}{2}$
Phosphorus, yellow	Lb.	35	@	40
Plaster of Paris	Bbl.	1.50	@	1.60
Potassium Bichromate	Lb.	30	@	34
Potassium Bromide	Lb.	85	@	87
Potassium Carbonate, calcined, 80 @ 85%	Lb.	25		
Potassium Chlorate, crystals	Lb.	20	@	22
Potassium Cyanide, bulk, 98–99 per cent	Lb.	nominal		
Potassium Hydroxide, 88 @ 92%	Lb.	30	@	38
Potassium Iodide, bulk	Lb.	3.40	@	3.50
Potassium Nitrate	Lb.	$14\frac{1}{2}$	@	$14\frac{3}{4}$
Potassium Permanganate, bulk, U. S. P.	Lb.	62	@	64
Quicksilver, flask	75 Lbs.	100.00		
Red Lead, American, dry	100 Lbs.	10.25	@	10.50
Salt Cake, glass makers'	Ton	12.00	@	15.00
Silver Nitrate	Oz.	81	@	82
Soapstone, in bags	Ton	10.00	@	12.50
Soda Ash, 58%, in bags	100 Lbs.	2.40	@	2.65
Sodium Acetate	Lb.	7	@	$7\frac{1}{4}$
Sodium Bicarbonate	100 Lbs.	2.75	@	3.50
Sodium Bichromate	Lb.	26	@	40
Sodium Chlorate	Lb.	22	@	23
Sodium Cyanide	Lb.	30	@	31
Sodium Fluoride, technical	Lb.	14	@	15
Sodium Hyposulfite	100 Lbs.	3.75	@	4.50
Sodium Nitrate, technical	100 Lbs.	2.95	@	3.15
Sodium Silicate, liquid, 40° Bé	Lb.	2.00	@	2.25
Sodium Sulfide	Lb.	$3\frac{1}{2}$	@	6
Sodium Bisulfite, powdered	Lb.	5	@	7
Strontium Nitrate	Lb.	25	@	28
Sulfur, flowers	100 Lbs.	3.30	@	3.85
Sulfuric Acid, chamber 66° Bé	Ton	20.00	@	22.00
Sulfuric Acid, oleum	Ton	nominal		
Talc, American, white	Ton	18.00	@	22.00
Terra Alba, American, No. 1	100 Lbs.	1.25		
Tin Bichloride, 50°	Lb.	$17\frac{3}{4}$	@	18
Tin Oxide	Lb.	60	@	61
White Lead, dry	100 Lbs.	9.00	@	9.50
Zinc Oxide	Lb.	9	@	$9\frac{1}{2}$
Zinc Chloride, U. S. P.	Lb.	45	@	50

ORGANIC CHEMICALS

Acetanilid	Lb.	55	@	60
Acetic Acid, 56 per cent	100 Lbs.	6.00	@	6.25
Acetic Acid, glacial, $99\frac{1}{2}$%	100 Lbs.	12.00	@	12.25
Acetone, drums	Lb.	$15\frac{1}{2}$	@	16
Alcohol, denatured, 190 proof	Gal.	69	@	71
Alcohol, Ethyl, non-beverage, 190 proof	Gal.	4.91	@	4.96
Alcohol, wood, 95 per cent, refined	Gal.	1 40	@	1.43
Amyl Acetate	Gal.	4 25	@	4.50
Aniline Oil	Lb.	30	@	34
Benzoic Acid, ex-toluol	Lb.	90	@	95
Benzene, pure	Gal.	33	@	35
Camphor	Lb.	3.60	@	3.75
Carbolic Acid, drums	Lb.	$14\frac{1}{2}$	@	$18\frac{1}{2}$
Carbon Bisulfide	Lb.	8	@	9
Carbon Tetrachloride, drums, 100 gals.		$11\frac{1}{2}$	@	12
Chloroform, U. S. P.	Lb.	30		
Citric Acid, crystals	Lb.	87		
Creosote, U. S. P.	Lb.	1 15	@	1.20
Cresol, U. S. P.	Lb.	15		16
Dextrine, corn (carloads, bags)	Lb.	6.19	@	6.41
Dextrine, imported potato	Lb.	17	@	18
Ether, U. S. P. 1880	Lb.	28	@	32
Formaldehyde	Lb.	30	@	35
Glycerin, dynamite, drums extra	Lb.	21		
Oxalic Acid, in casks	Lb.	30	@	34
Pyrogallic Acid, resublimed, bulk	Lb.	2.50	@	2.55
Salicylic Acid, U. S. P.	Lb.	55	@	60
Starch, corn (carloads, bags), pearl	100 Lbs.	5.97		
Starch, potato, Japanese	Lb.	8	@	$8\frac{3}{4}$
Starch, rice	Lb.	25	@	27
Starch, sago flour	Lb.	$7\frac{1}{2}$	@	9
Starch, wheat	Lb.	9		
Tannic Acid, technical	Lb.	80	@	95
Tartaric Acid, crystals	Lb.	74	@	$74^{1}/$

OILS, WAXES, ETC.

Beeswax, pure, white	Lb.			
Black Mineral Oil, 29 gravity	Gal.	20	@	22
Castor Oil, No. 3	Lb.	$19\frac{1}{2}$	@	20
Ceresin, yellow	Lb.	14	@	16
Corn Oil, crude	Lb.	18		
Cottonseed Oil, crude, f. o. b. mill	Lb.	$19\frac{1}{2}$	@	20
Cottonseed Oil, p. s. y.	Lb.	$20\frac{1}{2}$	@	21
Menhaden Oil, crude (southern)	Gal.	90	@	1.05
Neat's-foot Oil, pure	Gal.	1.65		
Paraffin, 118 to 120 m. p.	Lb.	$7\frac{3}{4}$	@	8
Paraffin Oil, high viscosity	Gal.	38	@	40
Rosin, "F" Grade, 280 lbs	Bbl.	17.95		
Rosin Oil, first run	Lb.	88	@	91
Shellac, T. N.	Lb.	1.25	@	1.30
Spermaceti, cake	Lb.	31		
Sperm Oil, bleached winter, 38°	Gal.	1.95	@	1.97
Spindle Oil, No. 200	Gal.	38	@	40
Stearic Acid, double-pressed	Lb.	$28\frac{1}{2}$		
Tallow, acidless	Gal.	1.65		
Tar Oil, distilled	Gal.	58	@	59
Turpentine, spirits of	Gal.	$1.64\frac{1}{2}$	@	1.65

METALS

Aluminum, No. 1, ingots	Lb.	32	@	33
Antimony, ordinary	100 Lbs.	9.75	@	9.90
Bismuth	Lb.	2.82		
Copper electrolytic	Lb.	$18\frac{1}{2}$	@	$18\frac{3}{4}$
Copper, lake	Lb.	19		
Lead, N. Y.	Lb.	7.00	@	7.20
Nickel, electrolytic	Lb.	55	@	56
Platinum, refined, soft	Oz.	135.00		
Silver	Oz.			
Tin	Lb.	$53\frac{1}{2}$	@	$53\frac{3}{4}$
Tungsten (WO_3)	Per Unit	7.00	@	10.00
Zinc, N. Y.	100 Lbs.	8.25	@	8.30

FERTILIZER MATERIALS

Ammonium Sulfate	100 Lbs.	6 50		
Blood, dried, f. o. b. New York	Unit	7.25	@	7.50
Bone, 3 and 50, ground, raw	Ton	32.00		
Calcium Cyanamide	Unit of Ammonia	nominal		
Calcium Nitrate, Norwegian	100 Lbs.	—		
Castor Meal	Unit	—		
Fish Scrap, domestic, dried, f. o. b. works	Unit	—		
Phosphate Rock, f. o. b. mine:				
Florida land pebble, 68 per cent	Ton	nominal		
Tennessee, 78–80 per cent	Ton	11.00	@	11.50
Potassium "muriate," basis 80 per cent	Ton	nominal		
Pyrites, furnace size, imported	Unit	$16\frac{1}{2}$	@	17
Tankage, high-grade, f. o. b. Chicago	Unit	7.00	@	10 00

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

AT ESCHENBACH PRINTING COMPANY, EASTON, PA.

Volume XII FEBRUARY 1, 1920 No. 2

Editor: CHARLES H. HERTY

Assistant Editor: LOIS W. WOODFORD *Advertising Manager:* G. W. NOTT

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Published monthly. Subscription price to non-members of the American Chemical Society, $6.00 yearly; single copy, 60 cents
Price per single copy to American Chemical Society members, 50 cents. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted
Entered as Second-class Matter December 19, 1908, at the Post Office at Easton, Pa., under the Act of March 3, 1879
Acceptance for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized July 13, 1918

All communications should be sent to The Journal of Industrial and Engineering Chemistry
Telephone: Vanderbilt 1930 Cable Address: Jiechem 35 East 41st Street, New York City
Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Secretary, 1709 G Street, N. W., Washington, D. C.

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THE SOCIETY'S PRESIDENT FOR 1920

WILLIAM ALBERT NOYES

William Albert Noyes, the newly elected president of the American Chemical Society, needs no introduction to its members. Editor of the *Journal of the American Chemical Society* from 1902 to 1917, during the years when it was advancing to its present position as one of the greatest journals of chemistry. Dr. Noyes will be identified by many of our members as the editor to whose guidance the Society entrusted its one organ of expression. When the Society recently launched its program to publish a series of chemical monographs on scientific and industrial topics of moment, it promptly made him editor-in-chief of the scientific series.

William Albert Noyes, President American Chemical Society

But to many others Dr. Noyes is identified even more markedly with the development and establishment on a firm basis of America's position in chemical research. The value of this development, from 1890 to 1915, was shown by the supreme test of the war with its problems of chemical warfare, production and creation. In the group of leaders in this development, Dr. W. A. Noyes stood shoulder to shoulder with Remsen, T. W. Richards, Nef, A. A. Noyes, Michael, and other university men. Acheson, Baekeland, Hall, Lovejoy, and other leaders in industrial chemistry, men whose research work commanded the admiration of the world of science, and kindled the enthusiasm of thousands of younger men who were ready when the call came. In token of his position among our research leaders Dr. Noyes was one of the earliest recipients of the Nichols Medal (1908) for his work (in collaboration with Dr. H. C. P. Weber) on the atomic weight of chlorine, and he has recently received the Willard Gibbs Medal for pioneer work on the electrochemical theory of valence. For many years his special field has been organic chemistry, centering in the chemistry of camphor and its derivatives, and in 1904 he gave the address on "The Present Problems of Organic Chemistry" at the gathering of the world's leading chemists in St. Louis. A member of the National Academy of Sciences since 1910, Dr. Noyes has recently been elected chairman of its Chemistry Section. He is also a member of the American Philosophical Society and of the American Academy of Arts and Sciences.

Many, especially among our younger members, will recall with pride that they are former pupils of Noyes, for he has not only been an eminent investigator and great editor, but also an active and inspiring teacher. His textbooks on general chemistry, organic chemistry and qualitative analysis are characterized by directness and clarity of exposition and sane and up-to-date presentation of facts and theories. Under the leadership of Dr. Noyes the department of chemistry at the University of Illinois has emerged from comparative obscurity to a position among our finest university laboratories. Noyes, with the support of a far-seeing university president, has made his department a beehive of research in practically every line of chemical effort.

We can appreciate the character of the man who has risen to leadership in our national Society. Honesty and vision have given purpose to his inquiring mind; courage has given point to its thrust; and an indefatigable working capacity has given him the power of successful accomplishment in every field he has touched.

The Society is to be congratulated on the fact that it has bestowed its brightest honor on one who has devoted the best years of his life to its service in bringing its senior Journal to a position of world authoritativeness, on one who has been and is a leader in research and teaching—on a true and loyal American—William Albert Noyes.

Chicago, Ill. Julius Stieglitz

EDITORIALS

CRITICAL DAYS

In a few short weeks public opinion, speaking through the Congress of the United States, will have declared its appraisement of chemistry as a national asset. This judgment is bound up in three important measures soon to be reported by committees which have given painstaking consideration to these matters. We refer to the Longworth bill which seeks to insure the permanency of our coal-tar chemical industry, the Bacharach bill which would provide a permanent domestic supply of the tools of the chemist, and finally the Army Reorganization bill which will determine the status of the Chemical Warfare Service either as a vigorous independent unit of our War Department or as a weakling appendage of some division of that Department.

On January 10, 1920, the very day of the proclamation of the ratification of the Treaty of Versailles, Marshal Foch gave words of warning in an interview from which the following statements are taken:

> It would be foolish to believe there will be no more war merely because we do not wish to fight. * * *
>
> War is not always avoidable. * * *
>
> If it is true two are necessary to make a fight, it is equally true the one best prepared will win. * * *
>
> There are ingenious people who believe that to leave the key in the door is the surest way to prevent entrance of thieves. I think it wiser to be ready for any unfavorable event. * * *
>
> War no longer may be called an art. It now is a science and an industry. * * *
>
> Those who wish to avoid violence cannot afford to ignore anything in the way of scientific and industrial progress.

It is our conviction that the final word of Congress will be such as to fill the hearts of chemists with renewed zeal and enthusiasm. Public opinion, however, must be informed regarding these measures in order to rouse itself to unmistakable expression, and that is the responsibility of the chemists of America. What is the state of public opinion in your neighborhood, fellow chemist? A word in advocacy *now* will be more valuable than whole volumes of regrets later. All together for American security and economic independence!

A SIGNIFICANT COMBINATION

Announcements of the formation of new corporations in the chemical industry with capitalizations running into millions have become so common in these hustling days that we are prone to take these developments as a matter of course and to give but slight thought to their meaning. However, peculiar and especial interest attaches to the announcement on January 9, 1920, of the formation of the Atmospheric Nitrogen Corporation, capitalized at $5,000,000. No details have been issued by the officers of the company as to the proposed lines of activity of the new organization. President E. L. Pierce, of the new company, announces that the Solvay Process Company has joined forces with the General Chemical Company in the matter of nitrogen fixation. As the establishment of an independent, self-supporting fixed nitrogen industry in America for the increase of crops in time of peace and as a preparedness measure for war is greatly to be desired, this announcement is of extreme economic importance. It is also announced from England that Brunner, Mond and Co., Ltd., operating the Solvay soda plants in that country, have arranged to take over the incomplete Haber plant started by the government and that they will operate the Haber process in addition to their ammonia soda business.

A word of explanation will make these announcements clear. When the various allied commissions visited the Haber ammonia process works at Oppau they found a small ammonia soda plant erected in connection therewith. This was first printed in a British government publication dated February 1919, which had only a very limited and confidential circulation. Later, the significance of the association of these two plants and its relation to the future of the nitrogen industry was clearly brought out by M. Georges Claude, first in a note in the *Comptes Rendus* of May 19, 1919, and later and more fully in *Chimie et Industrie* for August 1919.

In the Haber synthetic ammonia process, the chief item of expense is the cost and purification of the hydrogen required for the reaction

$$N_2 + 3H_2 = 2NH_3.$$

The cheapest known method of producing hydrogen in quantity for the Haber process and the one used at Oppau is illustrated by the following reactions for the production of water gas and for the treatment of this water gas with steam in the presence of a catalyst:

$$C + H_2O = CO + H_2 \qquad (1)$$

$$(CO + H_2) + H_2O = CO_2 + 2H_2 \qquad (2)$$

It will be observed at once that eleven tons of carbon dioxide are produced for every ton of hydrogen set free. For a long time this carbon dioxide was considered as a useless waste product, and such appears to have been the case in Germany until early in 1918. Some bright chemist, however, finally remembered that in the Solvay soda process thousands of tons of carbon dioxide are used each year and many hundred thousand tons of limestone burned for this specific purpose. A short study at once made plain that the ammonia industry and the soda industry for most civilized countries is or should be of the same order of magnitude and a further interesting interdependence was at once brought out.

The Solvay soda process is usually considered as involving the following reactions:

$$CaCO_3 + C\ (+\ O_2) = CaO + 2CO_2 \qquad (3)$$

$$NaCl + H_2O + CO_2 + NH_3 = NaHCO_3 + NH_4Cl \qquad (4)$$

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O \qquad (5)$$

$$2NH_4Cl + CaO = CaCl_2 + 2NH_3 + H_2O \qquad (6)$$

By adding the rich carbon dioxide from (5) to the much leaner gas from (3) a carbon dioxide of around 55 per cent CO_2 is obtained for use in (4). The waste carbon dioxide from the Haber process is much purer and varies from about 75 per cent, if nitrogen is mixed with the water gas, to approximately 90 per cent if it is not. One of the great drawbacks of the Solvay process is the waste of ammonia in recovery (6), and of lime and chlorine, as calcium chloride, the latter being a waste nuisance that is present at every ammonia soda plant. At the same time one of the problems of any plant fixing nitrogen as ammonia is to produce the ammonia in a form suitable for application to the soil. This is commonly done by neutralizing with sulfuric acid to form the sulfate. Any neutral, fixed, and nonhygroscopic salt of ammonia, of which there are few, would probably do as well. Georges Ville and others have shown that ammonium chloride, which is a more concentrated nitrogen product than the sulfate and meets the other requirements also, is equal to sulfate as a fertilizer, just as potassium chloride is as available for crops, with the possible exception of tobacco, as potassium sulfate.

Accordingly, a synthetic ammonia plant and a Solvay soda plant supplement each other perfectly when the above method of producing hydrogen is utilized. If the waste carbon dioxide, together with the ammonia, is passed into brine the products obtained at once are sodium bicarbonate and ammonium chloride, the one ready for sale or conversion into soda ash, the second ready for the fertilizer markets.

For the recovery of ammonium chloride in solid form, suitable for fertilizers, it seems that it will not be necessary to resort to evaporation, for Claude states that in collaboration with Mittau he has worked out an adaptation of the method of Schreib for alternative precipitation of the sodium bicarbonate and of the ammonium chloride, depending upon the very slight solubility of the ammonium chloride in cold solutions of neutral ammonium carbonate of appropriate concentration.

By the coördination of these two processes to meet America's needs for fixed nitrogen, there will result lower installation costs for both processes, the saving of several hundred thousand tons of sulfuric acid, several hundred thousand tons of lime, several thousand tons of coke, and the elimination of a waste product that has always been considered a nuisance. The saving made may be credited to either product at will.

Necessary information for the installation of the Haber process is at hand or is rapidly being acquired. The Chemical Foundation, Inc., has control of the Haber patents. A new day is evidently at hand for two fundamental chemical industries in America—nitrogen fixation and soda manufacture.

THE JOY AND THE SORROW OF M. I. T.

The juxtaposition of light and shadow in earthly affairs has been strongly illustrated during the past month at Massachusetts Institute of Technology. $8,000,000 was needed to enable that splendid institution to continue fittingly its work. Spurred on by the announcement that the mysterious "Mr. Smith" had again come to "Tech's" aid with an offer of one-half the needed amount, provided the other half were raised, there began a drive for the goal. As a part of the drive, a novel plan of coöperation with the industries was evolved. Details of a joint contract have been worked out by which the industries agree to contribute definite amounts annually for a period of five years. These funds are to be used chiefly to increase the salaries of the instructing staff. In return the Institute offers contributors the use of its libraries, files, and plant, the members of its staff are to be available as consultants, and a classification of its alumni and undergraduates, detailing special qualifications of each, is to be maintained. The plan is bold in its conception and may prove one of the most important steps of recent years in technical education. Its proponents look forward with confidence to the future and answer in advance objections which might be raised.

The net result of the drive was success, and a dinner followed where alumni and friends could voice their joy. At this dinner the identity of "Mr. Smith" was revealed, Mr. George Eastman, of Rochester, N. Y., whose contributions to this institution now total $11,000,000.

However, there was a vacant seat at the dinner, that of President R. C. Maclaurin, whose staunch spirit had supported and inspired every feature of that drive. Only a few days later came the announcement of his death. Just at the moment of his greatest triumph for the institution he loved so well he passed away.

Fortunate the institution which enjoyed for twelve years the far-seeing leadership of such a man as President Maclaurin and can still count as one of its most valuable assets the memory of all for which he stood.

STUDENT OPINION

The Bacharach bill passed the House of Representatives on August 2, 1919. This bill increases the duties on imports of chemical glassware, porcelain, and scientific instruments and repeals that clause of existing legislation which gives to educational institutions the right to import such articles free of duty.

In the debate on the bill Representative Kitchin, strongly opposing its passage, laid great stress upon the "poor, hard-working students in this country," and emphasized the point that no student or representative of the students had been heard by the Ways and Means Committee. Our own feeling all along has been that if student opinion could be ascertained, it would show a strong majority in favor of the bill. This, however, was a mere matter of opinion based upon the conviction that the spirit of independence is still strong in the hearts of young Americans.

Through the courtesy of Professor Pond of Stevens Institute we have been given opportunity to put the matter before the students in the chemistry courses of that institution. In our remarks we emphasized cold-bloodedly that this bill meant a tax upon the students of the country. We leaned over backward in the effort to avoid any plea for the bill. No reference whatever was made to the resolutions passed by the Council of the American Chemical Society, urging repeal of the duty-free privilege. We wanted no hasty judgment, and so the subject was left for discussion among themselves and for a vote at whatever time and in whatever manner they might decide upon.

To-day we received from the student chairman of the meeting the result of the ballot as it was taken by classes, on the Bacharach bill:

Class	Favor	Against	Per cent Favoring
Senior	66	11	86
Junior	113	15	88
Sophomore	133	18	88
Freshman	245	55	82
Total	557	99	85

We commend these figures to the subcommittee of the Senate Committee on Finance which is now considering the Bacharach bill. We believe that this judgment, deliberately expressed by the students of Stevens Institute, is thoroughly representative of student opinion throughout the country.

SAFETY IN SPEECH

To the scientist the approach of a newspaper reporter has long been a signal for withdrawal into a shell of silence. For this restraint he could not justly be blamed, for there stood before his memory the distorted condition in which an expert opinion ventured in an unguarded moment by some colleague had appeared in print.

There are times, however, when the scientist holds the responsibility of safely guiding public opinion. He should speak, and his views should be made known through the widest medium of reaching the public, namely, the press. The difficulty in the past has been the channel through which these views reached the make-up room of the newspaper.

In the hope of overcoming this difficulty, the A. C. S. News Service has just made an experiment, the success of which has proved so remarkable that it should be recorded, in the confident hope that when members of the American Chemical Society understand what is being attempted they will give the same generous measure of coöperation as was given recently by Dr. Reid Hunt of the Harvard Medical School.

It is not exaggeration to say that the recent extraordinary number of deaths from drinking wood alcohol presented the possibility of a national disaster. Quick, full, and responsible publicity was needed. In this situation Dr. Hunt was asked to prepare a statement which could be sent out over his name to the press of the country by our News Service. The request was promptly complied with; the material was put into newspaper shape by the technical manager, Mr. Harrington; and a few hours later the distribution through the mails was in progress.

Returns from the clipping bureaus show how broadly this material was utilized, in most cases in full as issued by the News Service, and as it appears on page 197 of this issue. The Associated Press, the United Press, and other news agencies gave the material immediate distribution. Not only was the matter used in the news columns, but it formed the basis of much sound editorial discussion. It is a significant fact that every clipping received to date not only quotes Dr. Hunt as authority for the statements, but says also that the bulletin was prepared at the request of the American Chemical Society.

Thus a national obligation and responsibility has been effectively met. Your equally generous coöperation is urged, if it should be requested.

NOTES

Last October the Société de Chimie Industrielle passed the six-thousand mark in its membership list. Congratulations and best wishes to this young organization, whose founders had the courage to launch it upon its career of usefulness during the darkest days of the war.

Still heartier will be the congratulations if some day the present two great French chemical societies are combined.

In St. Louis recently a jury disagreed in the suit brought by our Government against a manufacturer of saccharine and the matter will again have to go to trial. In France it was decided last fall to continue as a peace measure the war-time repeal of anti-saccharine legislation, the revenue from the government monopoly of this industry continuing to aid the national exchequer.

There is humor even in Congressional hearings, for example, this extract from the testimony of January 12, 1920, on the Longworth bill:

> Mr. Metz. On the contrary, I have stated my position here. I am a consumer. It is not selfish on my part, but the other men are selfish; that is the difference. It is the consumer I am looking out for. I have done that from the beginning.

Toy sets for chemical experiments are indicative of the present general interest in matters chemical. May it not be well, however, to offer the manufacturers of such toys, through a committee of the Society, expert advice on the character of experiments which may safely be placed in children's hands? Already one young lad has been severely burned by the breaking of a test tube in which he was boiling concentrated sulfuric acid.

We were not satisfied with our page of Market Reports, and even doubted its usefulness in a monthly publication, but inquiry among our readers developed the fact that it was of value to them. Beginning with this issue the list has been revised, a page has been added to include the new dye industry, and quotations on all items are given as of the beginning and the middle of the previous month, so that the trend of the market may be noted. It is hoped that these changes will increase the usefulness of this section.

THE CHEMICAL INDUSTRY AND TRADE OF JAPAN

By O. P. Hopkins, Washington, D. C.

Received January 3, 1920

The war has stimulated industrial development in Japan in a most remarkable manner, and no lines have been more favorably affected than those concerned with the production of chemicals and allied products. It is safe to say that the American chemical manufacturer is not quite so much interested at this moment in the markets offered for his goods in Japan as he is in the future competition he may expect from the Japanese manufacturer in the growing markets of the Far East and even in the Western Hemisphere.

The boom in the Japanese chemical industry resulted from the same circumstances that brought about a similar development in the United States—the cutting off of European supplies, with the consequent rise in prices, and the insistent demand for munitions at very high prices. The Japanese were even more unprepared than we were to meet the situation that arose when war was declared, and they have naturally not been able to achieve the same measure of success as we have. But in many lines they have made sound progress, and their present position is deserving of the most careful study.

Their efforts have been directed mainly toward the development of a coal-tar industry, the production of alkalies for the paper, glass, textile, and soap industries, progress in metal refining, and the greatest possible utilization of water power in electrochemical processes. The manufacture of iodine and potash from kelp, of glycerin, paints, fertilizers, the tanning of skins and hides, and many minor lines have also been pushed energetically. The match industry was well established before the war.

There are many factors that favor the present program. Water power is abundant, cheap, and well distributed throughout the industrial regions. Few concerns pay as high as two cents per kilowatt-hour and some pay less than one cent. The coal supplies are adequate, although not conveniently located. The price is somewhat higher at the pit-mouth than with us, and by the time the costly transportation is added, the price to the consumer is very high—$4.73 a metric ton at Yokohama, for instance, in 1913, and $17.80 in 1918. Certain raw materials are had in great abundance, either from Japanese sources or from easily accessible sources in nearby countries, such as sulfur, camphor, menthol, vegetable oils of all kinds, kelp, phosphate, lime, silica, and wood. The salt supply is something of a problem, as the government monopoly is considered by the manufacturers not to have worked out to the best advantage of the alkali industry, but a satisfactory supply is expected eventually. The attitude of the government may be considered a favorable factor, as every encouragement has been given the growing industries, including subsidies to one large company each in the dyestuff, medicinal, and glycerin industries. One of the most favorable factors is the low-priced labor, although it is well known that labor costs are not relatively so high in the chemical as in some other industries. But Japanese labor is very low priced, despite even war wages. Wages have not risen any more rapidly, proportionally, than in western countries, and while improvements in the standard of living may be expected, it is not reasonable to suppose that the standard will ever be so high as with us while there are so many millions to be fed, sheltered, and clothed in so small an area. The country is badly overpopulated. In this fact lies the "necessity" upon which the whole political program of the statesmen is based.

There are also unfavorable factors which tend to hold back the expansion of the chemical industry. The supply of technically trained men is inadequate, although a great many foreign engineers have been induced to come in. The failure of certain individual enterprises is attributed to faulty engineering. For the most part the laborers have had no experience that fits them for the new work, although there are exceptions, such as the facility with which ceramic workers adapt themselves to glass-making. This lack of trained chemists and laborers is a very serious one, but it is something that can be overcome in time. It should not be considered a permanent factor—witness the remarkable manner in which the Japanese have learned to manufacture the electrical equipment required to utilize their water power. Lack of equipment has also limited progress, as suitable outfits were difficult to buy abroad during the war, and manufacturing them at home has been a slow job. This is another shortcoming that can be remedied in time. A further obstacle in the way of some branches of the industry has been the methods used in selling to the new foreign markets. All sorts of irregularities have been charged to the exporters and much harm done which it will take a long time to undo. Business immorality is not of course a matter to be determined by geographical boundaries, and much can be said, and has been said, in extenuation of the faults of the Japanese trader, but at any rate the harm done in this direction is now well recognized by the Japanese themselves, and the government and commercial organizations are coöperating to remedy the trouble. Matches and glassware, for example, must now pass inspection before they can be exported.

The purpose of this paper is to bring together statistics of production and trade that will give the American manufacturer some definite idea of what the Japanese are actually accomplishing in the field of industrial chemistry. A study of the import statistics will also show what lines can be sold in Japan. A number of industries have been singled out for separate discussion. For the most part they are the lines to which the Japanese are paying particular attention, but it has been impossible to treat all such lines in this manner, as details for all are not available. As a matter of fact, it has been difficult to assemble the facts into an orderly treatment of the subject, for much of this business is new to Japanese economists, statisticians, and writers, and the sources of information still leave much to be desired. Even in the official statistics, the statisticians working on the production, import, and export returns have at times used different classifications, units, and arrangements. For this paper it was decided to use quantities wherever possible, even when that course did preclude interesting totals, for prices have varied so much that they now mean very little in such statistics.

Figures are from official Japanese statistics unless otherwise indicated. Some of the descriptive facts have been taken from Japanese trade papers, organs of commercial organizations, and the unofficial but authoritative Japan Year Book; some have been obtained from officials recently returned from Japan, and some are to be found in material published by the United States Bureau of Foreign and Domestic Commerce.

ACIDS

Not many details are available that bear on the production and use of acids in Japan. Abundant supplies of native sulfur and pyrites make it possible for manufacturers to supply the country's needs for sulfuric acid and to do some exporting. The production of hydrochloric acid increased from about 8,000,000 lbs. in 1913 to nearly 25,000,000 lbs. in 1917, but it evidently does not enter foreign trade, as no official figures for imports or exports are given. The domestic output of nitric acid went up from 1,077,100 lbs. in 1913 to 4,942,070 lbs. in 1917 (no foreign trade figures available). Imports of carbolic acid fell from 4,731,134 lbs. in 1917 to 2,950,867 lbs. in 1918. It has not been produced in large enough quantities to obtain notice in the official returns. Of the 6,993,760 lbs. of acetic acid produced in 1917, 5,632,007 lbs. were exported. There was a falling off in exports of about a million pounds in 1918. Boric, citric, oxalic, salicylic, and tartaric acids are imported in varying quantities, as shown in the complete table of imports.

CAMPHOR AND MENTHOL

More than half of the world's production of natural camphor comes from Formosa (now called "Taiwan" by the Japanese) and Japan proper. Wasteful methods of production and the greatly increased demands for the product have recently made it advisable for the Japanese government to regulate the exports by allocating supplies to the various consuming countries. The causes for the increased demand are well known, and the reasons assigned for the inability to meet the demands are scarcity of labor, the destruction of easily accessible trees, and the difficulties and dangers attending the exploitation of forests in the wilder sections of Formosa, where hostile savage tribes still make the camphor worker hesitate about sticking to his job even at higher wages than most other industries offer. Under government auspices, the situation is being very carefully studied and constructive plans put into operation for improving the output. Much planting of new trees is being done and a careful survey of all existing sources is going forward. It is also hoped that all districts now menaced by savages will soon be brought under control. In the meantime all the camphor companies have united to form one big company and expect to compete to better advantage for labor in the future.

The following figures will give a general idea of the magnitude of the industry and the export trade (crude, oil, and refined camphor have been lumped together without reducing them to a common basis):

	1913 Lbs.	1917 Lbs.	1918 Lbs.
Production	6,284,087	7,334,737	(1)
Exports	3,278,200	4,126,928	2,333,652

(1) Not obtainable.

The government is now discouraging the exports of crude camphor, with the idea that the country can profitably do its own refining. The war served to revive interest in the manufacture of celluloid, which, for some reason or other, had been languishing, and unmanufactured celluloid and such celluloid products as combs, hair pins, and toys are now exported in considerable quantities.

The menthol trade, which has virtually been controlled by the Japanese in times past, was hit rather hard by the war. Japanese exports reached their highest point in 1916, when sales abroad amounted to 511,168 lbs., and since then have declined. There has been an increasing tendency on the part of the farmers to cut down the acreage devoted to peppermint in favor of grain and beans, which pay better. In two of the principal districts the cut in acreage has amounted to 50 per cent during the last year.

DYESTUFFS

When the exports of dyes from Germany were shut off, Japan found herself in the same boat with the United States, England, and France; that is, with extensive dye-using industries and practically no domestic production of dyes to meet their demands. As a matter of fact, Japan was in a worse plight than any of the others, because there was practically no experience to fall back upon. She had to build from the ground up so far as raw materials, personnel, and equipment went.

In 1915 an act was passed to subsidize one company for the manufacture of dyestuffs, and under this act was organized the Japan Dyestuff Manufacturing Joint Stock Co., with 160,000 shares of $24.90 each. The government guaranteed dividends of 8 per cent, and there was a disposition at first on the part of unprotected manufacturers to fear the competition from this firm and resent the action of the government. In a short time, however, the demand for dyestuffs sent prices up to a point that brought them enthusiastically into the business, and early in 1916 it was announced unofficially that the total production of aniline oil by all companies was 60,000 lbs. a month. By the middle of 1918 there were 100 factories in existence, exclusive of small concerns manufacturing inferior goods, with a total capitalization of about $7,500,000.

The Japanese dye makers have naturally had difficulty in satisfying their customers in the matter of quality, and there has been much dissatisfaction on the score of prices also, but the fact of the matter seems to be that the staple dyes are coming forward in large quantities and that the industry seems pretty well established. The leading manufacturers have started a movement to induce the government to impose a high enough tariff wall to make certain that outside competition will not undo the progress made under the stimulation of war prices.

The United States now has the major portion of the import trade in aniline dyes and logwood extract, and is doing a considerable business in both lines. In the following table are shown Japanese imports from all countries for three different years. The supplies of aniline and artificial indigo in 1913 originated almost exclusively in Germany, while the logwood extract came largely from France. The natural indigo purchased in 1918 came from China.

Principal Imports of Dyes into Japan

	1913 Lbs.	1917 Lbs.	1918 Lbs.
Aniline dyes	9,738,863	832,947	2,538,725
Artificial indigo	2,186,513	1,910	143
Natural indigo	27,432	85,664	1,444,856
Logwood extract	955,992	1,649,205	3,588,288

It is the opinion of Japanese manufacturers that the future of American participation in the trade will depend upon the ability of Germany to supply her former customers at competitive prices, and that the future of both German and American exporters, and therefore of the Japanese dye manufacturers, depends to a considerable extent upon the attitude of the Japanese government on the tariff question.

FERTILIZERS

It is probably safe to say that fertilizers play a more vital part in the agriculture of Japan than in that of any other country in the world. For centuries the intensive cultivation of the soil has demanded their liberal use. Twenty-five years ago dependence was placed mainly on such "natural" manures as nightsoil, stable manure, and fish, and to some extent upon rice bran and cake from vegetable-oil presses. Then artificial fertilizers were gradually introduced and large quantities of Chilean nitrate, phosphate, ammonium sulfate, and bean cake were imported. Still later, the war stimulated home production of fertilizers and to-day enormous quantities of ammonium sulfate and superphosphates, as well as other chemical salts of minor importance, are manufactured by Japanese firms. Potash salts as such do not seem to play an important part in Japanese agriculture. Production of chemical fertilizers some time ago reached a point where exports on a considerable scale were made at fancy prices, but this development was considered detrimental to the interests of the country until such time as the home demand was really met, so the government stepped in and exercised a rigorous control over exports.

Before the war ammonium sulfate was imported from England to the extent of about 115,000 tons, but when this source was cut off, its production was undertaken successfully by the electrochemical plants, which had already made strides in the manufacture of calcium carbide and atmospheric nitrogen. The gas industry also produces important quantities as a by-product. At this writing the domestic product is high priced and some fear is felt that English supplies may injure the industry. Latest unofficial figures indicate that the domestic production is somewhat more than half the pre-war consumption. Prohibition of exports led some manufacturers to export calcium carbide, for which there has been a good outside demand.

Phosphate rock for the superphosphate industry is obtained from islands in the South Seas and the Indian Ocean. Production of the finished fertilizer has reached something like 500,000 tons a year, which is more than sufficient for home use, and export markets have become a necessity. Most of the surplus is sold in the Dutch East Indies and in Siberia.

The soy-bean cake and meal used so extensively as a fertilizer comes from oil mills in Manchuria and Japan. The consumption of this fertilizer amounts to more than 1,300,000 tons. It is exported to the Pacific Coast of the United States when shipping rates are normal, and the exporters hope to develop this trade further in the future.

Sodium nitrate comes from Chile. The fish and other animal products used as fertilizers are from domestic sources. Packing-house fertilizers, so extensively used in the United States, are not in evidence in Japan, as the people are not meat eaters. There are no statistics showing the quantities of nightsoil and stable manure used, but it is well known that the Japanese, like the Chinese, make the most of these materials.

So far as opportunities for American fertilizers in Japan are concerned, they will probably be limited in the future to packing-house products, specialized mixed fertilizers, and possibly sulfate of ammonia, if competition from English and Japanese producers can be met.

GLASS AND GLASSWARE

The removal of Belgium, Germany, and France from the glass trade in the Far East has stimulated the Japanese industry to a remarkable degree, and this is a line in which the Japanese seems certain to hold his own at least, even when the European competition returns. Recent developments are shown statistically in the following table:

	1913	1917	1918
Production	$2,914,036	$13,626,403	([1])
Imports	1,646,758	1,261,233	$1,223,614
Exports	1,652,791	6,669,672	8,007,614

[1] Not obtainable.

It is evident that export markets opened to the Japanese through the absence of European competition were the prime factor in this sudden development, and these markets are found chiefly in easily accessible Asiatic countries, although some of the product has found its way to the United States and other distant fields. The following official United

States statistics show how the trade with this country has been affected:

	1913	1917	1918
Imports from Japan	$9,053	$ 98,087	$351,713
Exports to Japan	9,117	623,014	500,232

The increased imports from Japan have consisted of beads and a large total still included under "all other" in the statistics of both governments. The increased exports to Japan have been largely plate glass, formerly supplied by Europe in qualities apparently not yet produced in sufficient quantities by Japanese manufacturers.

According to a statement recently prepared by the Far Eastern Division of the Bureau of Foreign and Domestic Commerce, the Japanese glass manufacturers have a decided advantage over their competitors in the matter of wages, and the laborers are said to adapt themselves readily to the industry because of previous experience in pottery making and similar lines. The average daily wage in glass factories in 1917, according to this statement, was 38 cents for males and 17 cents for females over 15 years of age, and 14 cents for males and 11 cents for females under that age. During the war large quantities of soda ash have been imported from the United States, but the domestic production of soda ash and sodium sulfate has rapidly increased, as explained elsewhere in this paper. The silica used in a large factory having an output of 100,000,000 sq. ft. of window glass a year is obtained from Korea and Anam and is said to be of excellent quality. It is interesting to note that the machinery in this factory is practically all driven by electric power. Much of the machinery in the larger factories is of American manufacture. The latest production figures are for 1917, but the expansion of the industry has continued since that date, according to later but unofficial reports.

MATCHES

Matches are one of the most important of the Japanese chemical manufactures, and the bulk of the production goes into foreign trade. Before the war the value of the match exports was about half that of the total for all chemicals and chemical manufactures; since then it has dropped down to about 40 per cent of that total. The following summary will give some idea of the size of the industry and the extent to which the product goes into foreign trade:

	1913 Gross	1917 Gross	1918 Gross
Production	51,731,010	52,531,551	(1)
Exports	44,009,245	44,150,011	39,467,420

[1] Not obtainable.

The industry supplies all domestic needs, and, with the exception of phosphorus, depends upon domestic materials. China, India, and other Asiatic countries take most of the exports, although they have found their way to America and Europe since the war started. The cost of labor has gone up in recent years, but the price of matches has advanced even more rapidly, as is shown by the fact that while exports have decreased somewhat in quantity, they have doubled in value. The low cost of labor is the most important factor in the success of the Japanese match industry, for the product is admittedly inferior in quality. The Japan Year Book confesses that the boxes and splints are weak and liable to break, while the friction surface is easily affected by dampness. This same authority states that Japanese matches are sold in Chinese and other nearby Asiatic markets at about 45 per cent less than their rivals.

As this matter of wages is important in appraising the chemical industries of Japan, it will be worth while to devote a little space here to a study of that phase of the match industry, as some figures given in the Industrial Census (in Japanese) make it possible to compare establishments with five or more operatives with American establishments included in the census of 1914. Wages, of course, have gone up in both countries since that time, but if it is borne in mind that the rise has been somewhat more rapid in this country than in Japan, a general idea of the present relative wage costs in the two countries can be formed. The comparison for 1914 follows:

	UNITED STATES	JAPAN
Wage earners:	3,800	17,677
Over 14 years:		
Male	....	4,075
Female	....	10,972
Under 14 years:		
Male	....	538
Female	....	2,092
Wages	$1,757,975	$752,258
Average wage	$463	$43
Horsepower	7,465	335
Production:		
Gross[1]	49,050,229	60,315,973
Value	$12,556,279	$9,120,562
Average production:		
Gross per wage earner	12,908	3,412
Gross per wage dollar	28	80
Average value of product:		
Per wage earner	$3,304	$516
Per wage dollar	$7.14	$12.12
Wages per 1,000 gross	$35.84	$12.47

[1] For United States, estimated by the United States Tariff Commission.

PAINTS

Japan is not a very great paint-consuming country, little being used on such things as houses and fences, yet the sudden demand for paints in the shipbuilding industry and the high prices offered in other Far Eastern countries have brought into being a considerable industry. Even the imports of shipsbottom paints have fallen off recently, and the decline in imports of other paints has been most striking. On the other hand, exports have increased from less than half a million to more than 15,000,000 lbs. since the war started, as the following summary shows:

	1913 Lbs.	1917 Lbs.	1918 Lbs.
Imports:			
Ship's-bottom	547,091	500,026	376,062
Other	1,774,597	471,585	264,888
Exports	474,708	2,420,850	15,034,236

There are no official statistics of paint production in the country. It is known that materials are to be found at home or in nearby China, although something like 52,000 gal. of turpentine oil were imported in 1918, almost entirely from the United States.

PAPER

Two general classes of paper are produced in Japan—Japanese and "European." The former has been made for centuries and is especially adapted to Japanese and Chinese needs. The latter is a comparatively new product, the manufacture of which has been greatly stimulated by the high war prices. It meets a growing demand at home and markets abroad are eagerly sought. China, Kwantung Province, and Hongkong take about 60 per cent of the exports of machine-made paper, which have been increasing rapidly. During the war India also became prominent as an importer of this paper. Good grades of printing paper are still imported, however, and in the absence of effective competition from England, the United States has become the chief source of supply.

A statistical summary of the situation follows:

	1913	1917	1918
Production:			
"European"	$11,455,823	$29,490,458	(1)
Japanese	10,425,814	18,069,209	(1)
Imports	3,604,262	2,035,693	$4,678,954
Exports:			
"European"	943,381	7,038,377	12,481,933
Japanese	598,604	977,090	1,695,530

[1] Not obtainable.

The timber resources of Japanese Saghalien and Hokkaido have made possible a rapid development of the pulp industry under the stimulus of war prices, as the following figures show:

	1913 Tons	1917 Tons	1918[1] Tons
Production	85,050	189,350	231,550
Imports	53,850	18,050	32,200
Exports	.....	4,150	?
Consumption	138,900	201,550	263,750

[1] 1918 production total on authority of Japan Paper Guild.

Japanese enthusiasts believe that eventually enough pulp will be made at home to meet all domestic needs, and that all foreign competition can be met in spite of the rising cost of labor and materials. It is a difficult matter to determine costs in this industry, but the following figures per 100 lbs. of pulp in a single large mill will be of interest (they are from the "Keizai Shimpo" for October 18, 1919):

	1915	1918 (August)
Mechanical pulp:		
Wood	$0.773	$1.780
Labor, including bleaching	0.100	0.670
Power	0.205	0.410
Miscellaneous	0.067	0.135
TOTAL	1.145	2.995
Sulfite pulp:		
Wood	1.250	2.855
Sulfur	1.120	0.188
Coal	0.023	0.033
Labor	0.125	1.190
Power	0.250	1.200
Miscellaneous	0.085	0.173
TOTAL	1.853	5.639
Bleaching sulfite pulp:		
Bleaching powder	0.340	0.575
Labor	0.025	0.035
TOTAL	0.365	0.610

Detailed statements covering the recent developments in the Japanese paper industry have been printed by the United States Bureau of Foreign and Domestic Commerce.

SOAP AND GLYCERIN

With the unlimited supplies of oils available it is not surprising that the Japanese have turned to soapmaking on a large scale. It is not possible to show the development by quantity, as different units are used for different soaps and for production, imports, and exports, but the following values will be better than nothing:

	1913	1917	1918
Production	$3,195,650	$9,744,127	(1)
Imports	78,883	57,632	$ 70,367
Exports	754,013	1,913,165	2,301,119

[1] Not obtainable.

A factory established in 1913 by a well-known English company has been producing soap on a large scale, including the finest grades of toilet soap. The unlimited markets that can be developed among the hundreds of millions of Asia seem to assure a prosperous future for the Japanese industry. At present the exports go chiefly to China, with important quantities to the Dutch East Indies.

No production figures are available for glycerin, but it is known that the output is increasing and the imports falling off. The 600,000 lbs. imported in 1918 was the semi-refined and refined product.

SODA AND BLEACHING POWDER

Caustic soda, soda ash, sodium sulfate and bleaching powder are all being turned out on an increasing scale by the Japanese to meet the demands of the soap, glass, and paper industries. A handicap in the past has been the high price of salt, which is a government monopoly, but recent concessions have been made in that respect as a result of heavy pressure brought to bear by the manufacturers. Details are difficult to get hold of, but the following statistics will help to explain the situation:

	1913 Lbs.	1917 Lbs.	1918 Lbs.
Caustic soda:			
Production	9,535,621	19,979,742	(1)
Imports	26,810,066	47,877,323	16,350,847
Exports	......	881,031	1,455,815
Soda ash:			
Production	4,756,402	7,597,771	(1)
Imports	68,521,861	98,060,756	124,159,672
Sodium sulfate:			
Production	3,138,682	18,657,527	(1)
Bleaching powder:			
Production	33,114,094	47,528,123	(1)
Exports	2,235,591	14,261,615	10,904,580

[1] Not obtainable.

It can be assumed from the foregoing figures that Japan is rather a long way from being independent so far as these three salts go, and that therefore American exporters can expect to find markets for some time to come. Before the war the imports came mostly from England, but the United States is now the chief factor. In soda ash, England predominated until 1917, but in 1918 America took the lead. The newer Japanese plants use electrochemical processes, but a number of the older concerns use the LeBlanc process. A plant has been established in Manchuria. where salt is cheap.

SULFUR

Japan is blessed with extensive deposits of sulfur and recovers enough of it each year to supply her own needs and to export extensively to Australia, British India, and other points in the east. Production and exports are shown by the following figures, which are supplemented with production figures for iron pyrites:

	1913 Lbs.	1917 Lbs.	1918 Lbs.
Sulfur:			
Production	131,059,061	260,329,009	156,634,240[1]
Exports	119,613,792	188,375,054	119,263,386
Iron pyrites:			
Production	252,586,826	267,559,347	(2)

[1] Estimated from official returns for the first 6 mo.

[2] Not obtainable.

The war stimulated the production of sulfur, but by 1918 high freight rates and transportation difficulties had cut down exports and discouraged production.

STATISTICS OF PRODUCTION

The statistics of production contained in the following table have been compiled from official reports of the Japanese Department of Agriculture and Commerce. As a whole, the table will give a fairly definite idea of the recent developments in the chemical and allied industries, although a number of branches will be found missing, presumably because they are of minor importance, or because they are so new that data have yet to be collected.

JAPANESE PRODUCTION OF CHEMICALS AND ALLIED PRODUCTS

ARTICLES	QUANTITY PRODUCED 1909	1913	1917
Acetone, lbs	(1)	(1)	728,900
Acids:			
Acetic, lbs	(1)	(1)	6,993,760
Hydrochloric, lbs	3,989,409	7,748,555	24,951,527
Nitric, lbs	1,160,333	1,077,100	4,942,070
Sulfuric, lbs	150,251,336	413,613,139	741,039,167
Alum, lbs	7,455,051	12,464,338	22,059,722
Ammonium sulfate, lbs[2]	1,847,349	1,818,658	24,122,051
Bleaching powder	14,453,362	33,114,094	47,528,123
Camphor:			
Crude, lbs	1,111,073	1,292,267	1,299,767
Oil, lbs	1,363,944	2,231,538	2,451,096
Refined, lbs	1,101,345	2,760,282	3,583,874
Fertilizers, artificial:[3]			
Animal, lbs	(1)	297,946,698	296,785,631
Vegetable, lbs	(1)	495,647,166	895,563,490
Mineral, lbs	(1)	1,207,959,705	1,102,234,108
Superphosphate, lbs	.....	1,132,838,096	982,192,275
Double superphosphate, lbs	.....	.....	5,945,279
Ammonium sulfate, lbs	.....	35,349,130	89,711,450
Potassium sulfate, lbs	.....	11,431,500	1,269,464
Calcium cyanamide, lbs	.....	9,101,529	8,559,569
Potash salts, lbs	.....	1,542,730	2,478,240
Other, lbs	.....	17,696,720	12,077,831
Mixed	.....	559,066,581	459,229,775
Iodine, lbs	76,773	152,566	484,138
Iron pyrites, lbs	47,416,891	252,586,826	267,559,347
Peppermint:			
Crude, lbs	226,899	803,040	1,094,711
Menthol crystals, lbs	147,921	258,060	561,843
Oil, lbs	142,182	272,006	564,964
Potash:			
Iodide, lbs	153,457	158,234	222,150
Chlorate, lbs	.....	.....	13,294,721
Chloride, lbs	1,044,011	4,451,967	19,466,656
Soda:			
Ash, lbs	2,892,835	4,756,402	7,597,771
Caustic, lbs	8,378,257	9,535,621	19,979,742
Sulfate, lbs	2,420,833	3,138,682	18,657,527
Sulfur, lbs	81,349,740	131,059,061	260,329,009
Wood spirit, gal	(1)	(1)	281,185
Candles, lbs	(1)	(1)	22,255,234
Glass	$2,088,940	$2,914,036	$13,626,403
Lacquer, lbs	553,352	664,245	714,914
Matches, gross	49,972,039	51,731,010	52,531,551
Oils:			
Petroleum, gal	78,964,394	80,705,957	119,706,578
Fixed vegetable	(1)	(1)	$18,998,865
Volatile	(1)	(1)	$112,088
Paper:			
Japanese	$9,072,837	$10,425,814	$18,069,209
"European"	$7,051,340	$11,455,823	$29,490,458
Soap:			
Toilet	$1,298,377	$2,484,678	$4,712,541
Industrial	$ 114,726	$167,930	$493,315
Laundry and other	$ 492,614	$543,042	$4,538,271
Sugar:[4]			
Jaggery, lbs	116,386,420	112,303,332	179,276,939
Muscovado, lbs	26,911,705	34,696,008	76,177,965
Brown, lbs	171,884	7,905,413	27,414,464
White, lbs	1,130,533	.....	.....
Waxes:			
Unbleached, lbs	18,967,887	12,935,334	15,816,499
Refined, lbs	9,900,716	10,263,120	11,168,734

[1] Not shown separately.
[2] Year ended March 1918.
[3] Figures for 1914 and 1917.
[4] Figures for 1910, 1913, and 1917.

STATISTICS OF IMPORTS

The imports statistics given in the following table are based upon the annual returns of the Japanese Department of Finance. Only principal countries of origin are given.

JAPANESE IMPORTS OF CHEMICALS AND CHEMICAL PRODUCTS

CHEMICALS, DRUGS, ETC.	1913	1917	1918
Acids:			
Boric, lbs	1,185,000	788,875	1,019,638
United Kingdom	326,933	641,468	513,425
United States	2,189	147,396	506,211
Germany	711,471	.....	.....
Carbolic, lbs	978,598	4,731,134	2,950,867
United States	.....	4,715,000	2,573,409
Germany	409,118	.....	.....
Citric, lbs	62,662	99,790	36,302
United Kingdom	32,061	83,303	17,102
Italy	.....	7,840	2,688
United States	.....	7,975	6,169
Germany	27,235	.....	.....
Oxalic, lbs	(1)	51,292	366,505
United Kingdom	.....	13,492	212,705
United States	.....	22,450	153,800
Salicylic, lbs	320,868	90,377	516,292
United States	.....	88,138	485,163
United Kingdom	2,241	2,239	31,129
Germany	290,294	.....	.....
Tartaric, lbs	159,380	341,170	269,086
United Kingdom	122,708	217,125	89,274
France	1,120	64,797	72,319
Italy	4,409	44,063	84,669
United States	.....	15,185	2,239
Germany	25,201	.....	.....
Alcohol, gal	6,602	506	5
United States	112	73	5
Germany	4,827	.....	.....
Alum, lbs	(1)	572,950	110,179
China	.....	572,300	71,795
Ammonium carbonate, lbs	433,757	982,073	299,854
United Kingdom	416,532	833,022	297,299
United States	.....	149,051	2,595
Germany	11,605	.....	.....
Ammonium chloride, lbs	1,095,218	904,430	224,244
United Kingdom	646,198	887,562	217,963
United States	251	13,935	5,581
Germany	448,748	2,933	.....
Bismuth subnitrate, lbs	31,463	6,868	1,599
United States	1,000	6,668	1,149
Germany	17,245	.....	.....
Calcium acetate, lbs	9,033,606	255,326	1,368,479
United States	9,033,578	255,326	1,360,688
Germany	28	.....	.....
Fertilizers:			
Ammonium sulfate, lbs	245,858,923	33,289,035	2,400,039
United Kingdom	230,534,365	24,743,532	561,253
Australia	4,155,888	2,906,265	1,771,987
Kwangtung Prov	307,016	4,951,139	66,668
United States	.....	225,268	.....
Bone dust, lbs	(1)	.....	42,574,107
China	.....	.....	24,217,068
British India	.....	.....	11,515,136
Kwangtung Prov.	.....	.....	6,627,754
Sodium nitrate, lbs	58,919,948	121,443,199	107,818,225
Chile	(1)	121,215,534	106,910,898
British India	(1)	.....	896,014
United States	(1)	224,004	745
Bean cake, lbs	(1)	2,185,407,850	2,530,188,786
Kwangtung Prov	.....	1,289,574,438	1,691,808,703
China	.....	460,733,075	353,281,592
Asiatic Russia	.....	63,708,318	11,048,197
Cottonseed cake, lbs	(1)	63,558,313	102,821,921
China	.....	63,558,313	102,325,880
Rapeseed cake, lbs	(1)	99,110,886	58,828,079
British India	.....	34,358,499	526,596
China	.....	64,725,267	57,997,117
Other oil cake, lbs	(1)	22,236,611	22,001,417
Asiatic Russia	.....	2,812,348	121,034
China	.....	12,488,829	14,504,078
Kwangtung Prov	.....	2,386,018	1,976,620
Glycerin, lbs	1,892,785	887,997	600,464
United Kingdom	1,251,486	724,243	45,113
United States	.....	133,387	518,132
Germany	588,273	.....	.....
Phosphorus:			
Red, lbs	455,630	260,644	129,839
United Kingdom	76,767	259,905	660
Germany	121,632	.....	.....
Yellow, lbs	377,682	47,589	.....
United Kingdom	254,504	31,979	.....
United States	.....	15,610	.....
Germany	105,201	.....	.....
Potash:			
Bichromate, lbs	591,945	584,688	221,615
United States	408,640	584,688	221,615
Germany	10,930	.....	.....
Bromide, lbs	92,701	3,410	335
United States	3,926	3,300	333
Germany	86,515	.....	.....
Chlorate, lbs	7,527,720	235,244	67,201
France	2,436,664	211,741	67,210
United States	.....	23,503	.....
Germany	3,071,533	.....	.....
Cyanide, lbs	1,100,671	652,165	607,810
United Kingdom	553,525	651,717	605,958
Germany	544,391	.....	.....
Nitrate, lbs	1,291,351	174,424	1,680,022
China	.....	149,185	1,131,434
Germany	1,280,215	.....	.....
Soda:			
Ash, lbs	68,521,861	98,060,756	124,159,672
United States	8,979	54,382,470	76,709,247
United Kingdom	68,510,677	40,880,290	46,983,738
Germany	2,205	.....	.....
Bicarbonate, lbs	9,910,039	6,881,352	7,331,829
United Kingdom	9,882,581	6,548,997	3,627,901
United States	112	220,405	3,662,187
Germany	27,346	.....	.....
Borate, lbs	1,401,041	3,373,388	2,348,931
United Kingdom	856,137	3,156,684	2,083,045
United States	148,640	216,704	265,887
Germany	396,274	.....	.....
Caustic, crude, lbs	26,810,066	47,877,323	16,350,847
United States	361,495	47,255,852	15,024,902
United Kingdom	26,412,689	603,804	789,976
Germany	32,501	.....	.....
Cyanide, lbs	.....	535,820	1,576,669
United Kingdom	.....	524,734	1,553,261
United States	.....	11,086	23,308
Germany	.....	.....	.....

[1] Not shown separately.

[1] Not shown separately.

Apanese Imports of Chemicals and Chemical Products (*Continued*)

Chemicals, Drugs, Etc. (*Concluded*)	1913	1917	1918
Peroxide, lbs	392,083	55,345	21,826
United Kingdom	83,442	30,213	7,275
Sweden	.....	17,334	.....
Italy	.....	7,275	14,551
Germany	117,259	.....	.....
Tanning materials:			
Galls, oak bark, and similar tanning materials, lbs	3,646,810	13,351,834	10,861,048
Cape Colony and Natal	.....	7,166,922	3,215,980
British India	223,860	4,238,570	1,558,106
China	590,860	997,863	589,460
Argentina	....	393,422	68,281
United States	2,012,742	195,033	1,674,070
Australia	273,871	179,004	1,308,854
Africa, n. e. s.[2]	.....	.....	1,505,610
Germany	225,492	.....	.....
Catechu and other tanning extracts, lbs	6,049,553	10,415,490	7,744,914
Argentina	88,185	3,858,817	180,049
Dutch East Indies	1,186,804	3,027,173	2,299,574
Straits Settlements	1,000,390	1,844,674	2,817,730
British India	37,703	668,764	1,508,436
China	20,663	546,352	6,667
Cape Colony and Natal	....	158,600	91,030
United Kingdom	507,204	111,936	388,203
United States	910,604	110,230	452,724
Germany	1,382,930	.....	.....
Drugs, medicines, etc.:			
Alcoholic medicinal preparations, gal	6,927	9,227	11,697
United Kingdom	4,774	7,536	9,872
United States	1,461	1,619	1,611
Germany	556	.....	.....
Antifebrin, lbs	88,747	105,151	204,613
United States	.....	94,960	201,009
Germany	46,755	.....	.....
Antipyrin, oz	731,694	54,359	94,259
France	75,818	29,879	33,903
Switzerland	25,832	13,141	36,748
United Kingdom	.....	9,732	23,608
Germany	630,044	.....	.....
Aromatic chemicals	$24,990	$26,454	$112,861
United Kingdom	5,383	16,397	48,389
United States	.....	6,648	53,412
Cocaine, oz	52,228	90,049	45,634
United Kingdom	1,763	30,426	17,356
United States	.....	30,404	15,228
France	.....	14,473	6,298
Holland	2,500	13,746	1,095
Germany	47,965	.....	.....
Formalin, lbs	946,562	571,865	730,840
United States	.....	534,957	724,943
Germany	535,976	.....	.....
Guaiacol carbonate, lbs	27,879	258	200
Switzerland	3,737	221	.....
Kwangtung Prov.	.....	30	.....
Germany	12,927	.....	.....
Milk sugar, lbs	427,003	65,743	499,816
United States	.....	24,530	499,373
United Kingdom	51,551	22,400	.....
Kwangtung Prov.	.....	12,998	.....
Morphine, oz	91,128	600,229	165,087
United Kingdom	73,303	598,749	119,722
Germany	17,327	.....	.....
Perfumed waters, lbs.	87,218	76,046	62,147
France	55,874	49,104	25,985
United Kingdom	10,668	24,630	29,430
Germany	8,047	.....	.....
Quinine, oz	253,829	513,763	452,799
Dutch East Indies	180,819	503,683	415,523
Santonin, lbs	4,492	1,697	3,665
Russia	.....	1,157	3,556
United States	.....	463	110
United Kingdom	1,282	77	.....
All other chemicals, drugs, etc	$1,665,673	$2,441,177	$4,855,881
United States	97,110	1,296,113	2,306,812
United Kingdom	172,409	353,466	397,925
China	97,933	249,762	485,885
British India	22,393	83,420	277,318
France	35,847	91,197	51,688
Peru	.....	67,393	331,127
Germany	1,049,996	11,018	3,845
All other preparations or compds. of chemicals, drugs, etc	$173,248	$245,336	$268,743
United Kingdom	29,344	39,329	24,682
France	13,320	19,509	4,517
Switzerland	2,334	19,195	9,190
Germany	68,901	1,635	.....
United States	57,916	160,881	228,287
Dyes, Paints, Etc.:			
Aniline dyes, lbs	9,738,863	832,947	2,538,725
United States	.....	337,115	1,841,808
Germany	8,585,797	279,987	462,445
Switzerland	662,861	160,898	165,782
France	269,749	21,876	14,398
Holland	23,035	14,201	.....
United Kingdom	178,373	4,462	31,442
Other coal-tar dyes, lbs.	(1)	13,978	29,840
Germany	(1)	13,978	10,599
Aniline salts, lbs	648,730	1	175,713
United States	.....	1	175,713
United Kingdom	138,338	.....	.....
Germany	360,644	.....	....

[1] Not entered.

Japanese Imports of Chemicals and Chemical Products (*Continued*)

Dyes, Paints, Etc. (*Concluded*)	1913	1917	1918
Indigo:			
Natural, lbs	27,432	85,664	1,444,856
British India	25,450	56,162	1,310,025
Dutch East Indies	1,214	29,502	122,632
Artificial, lbs	2,186,513	1,910	143
Germany	1,974,432	1,870	69
Logwood extract, lbs	955,992	1,649,205	3,588,288
United States	4,508	1,303,737	3,483,008
France	878,149	283,507	61,571
United Kingdom	.....	61,865	42,757
Germany	73,223	.....	.....
Oxide of cobalt, lbs	40,169	116,347	103,598
United Kingdom	39,284	108,984	10,601
United States	884	7,363	92,998
Saffron, lbs	5,025	3,329	3,758
France	3,148	1,720	3,024
Spain	1,190	1,609	.....
Germany	485	.....	.....
Ultramarine blue, lbs	322,406	91,316	167,165
United States	.....	50,908	144,063
United Kingdom	30,384	22,908	8,816
France	14,393	17,084	14,286
Germany	258,467	.....	.....
Carbon black, lbs	356,819	407,285	971,718
United States	325,287	407,044	968,024
Germany	7,449	.....	.....
Lacquer, lbs	1,587,784	1,657,637	2,064,038
China	1,542,734	1,616,253	2,038,927
French Indo-China	45,036	41,371	21,121
Liquid gold, silver platinum, oz	44,923	20,210	23,836
United States	7,791	16,410	21,482
United Kingdom	10,284	3,800	2,200
Germany	24,794	.....	.....
Ship's-bottom paints, lbs.	547,091	500,026	376,062
United Kingdom	437,075	390,503	218,877
United States	98,209	108,291	146,971
Other paints, lbs	1,774,597	471,585	264,888
United States	81,784	139,781	176,322
United Kingdom	1,621,299	327,613	88,095
Germany	24,355	.....	.....
Varnishes, lbs	603,102	741,227	311,381
United States	188,891	493,946	286,620
United Kingdom	376,500	246,345	22,973
Germany	23,647	.....	.....
White lead, red lead, and litharge, lbs	130,061	14,855	18,256
United States	13,298	8,700	112
United Kingdom	103,191	6,151	16,984
Germany	12,582	.....	.....
Zinc white	(1)	96,258	493,175
United Kingdom	.....	22,407	17,426
Printing ink, lbs	334,613	116,105	212,740
United States	240,692	88,033	188,031
United Kingdom	26,895	27,336	22,901
Germany	59,998	.....	.....
Other ink, lbs	212,870	11,186	59,580
United States	90,117	4,989	23,188
United Kingdom	121,850	4,963	33,053
France	257	1,188	3,315
Germany	646	46	.....
All other dyes and pigments	$259,301	$267,594	$552,824
United Kingdom	56,798	119,400	125,891
United States	8,916	91,906	349,998
China	5,421	28,314	42,186
France	24,058	15,509	7,468
Germany	135,373	3,036	.....
All other coatings and fillers	$91,116	$84,308	$92,111
United States	24,427	61,109	74,235
United Kingdom	46,122	21,783	16,860
France	1,950	580	.....
Germany	12,208	.....	.....
Oils, Fats, Waxes, and Manufactures thereof:			
Oil-bearing materials:			
Soy beans, lbs	235,521,849	185,616,327	258,322,752
Peanuts, lbs	.....	3,718,040	14,060,680
Sesame, lbs	13,129,316	12,085,122	25,795,264
Perila ocimoide, lbs.	9,883,760	17,604,130	17,055,967
Rape and mustard, lbs.	35,573,334	78,439,933	127,505,661
Linseed, lbs	.....	8,269,715	14,528,942
Hempseed, lbs	.....	17,110,470	7,131,334
Cottonseed, lbs	26,540,382	47,405,818	32,696,701
Copra, lbs	5,639,797	89,678,340	165,184,726
Vegetable oils:			
Castor oil, lbs	970,148	730,040	1,044,503
China	426,159	405,706	758,860
Kwangtung Prov.	185,338	77,710	11,158
United States	.....	5,740	16,088
Germany	37,765	.....	.....
Coconut oil, lbs	1,128,489	2,003,237	681,319
Straits Settlements	107,978	1,372,548	113,158
Linseed oil, lbs	582,257	147,103	438,426
United Kingdom	509,553	72,572	7,822
China	.....	59,730	327,929
United States	11,320	13,045	231
Germany	5,122	.....	.....
Olive oil, lbs	197,036	118,070	140,595
France	121,436	47,944	20,929
Italy	30,489	35,563	1,746
United States	3,167	14,610	37,515
Spain	2,493	8,820	17,637
Germany	35,229	.....	.....
Soy-bean oil, lbs	6,249,522	1,024,240	2,633,915
Turpentine oil, gals.	38,731	51,690	88,047
United States	38,100	51,642	88,026
Vegetable tallow, lbs.	.....	20,915	5,483

[1] Not shown separately.

JAPANESE IMPORTS OF CHEMICALS AND CHEMICAL PRODUCTS (*Continued*)

OILS, FATS, ETC. (*Concluded*)	1913	1917	1918
Mineral oils:			
Crude, gal.	3,519,619	3,242,766	1,271,108
United States	159	3,242,766	1,127,825
Gasoline, gal.	296,065	1,139,712	2,757,799
United States	295,360	383,594	321,339
Dutch East Indies	.....	345,512	2,404,460
Kerosene, gal.	48,174,840	19,426,787	23,276,881
United States	33,145,387	17,943,857	19,752,947
Dutch East Indies	15,029,453	1,482,791	3,513,369
Mineral colza, gal.	565,449	537,382	291,254
United States	565,409	537,382	291,254
Paraffin wax, lbs.	17,902,123	23,780,672	34,040,882
British India	3,650,442	7,495,273	8,069,098
Dutch East Indies	636,979	9,239,780	15,385,960
United States	7,252,562	6,621,634	9,995,959
Vaseline, lbs.	910,291	689,837	576,290
United States	13,221	659,074	576,290
United Kingdom	127,341	28,117	.....
Other mineral, lbs.	19,572,190	15,767,900	33,787,687
United States	18,101,324	15,709,430	33,720,643
Dutch East Indies	23,246	.....	97
Tallow, beef, lbs.	9,943,623	16,813,550	20,056,708
China	6,659,223	9,390,834	8,756,427
Australia	2,747,315	7,298,393	10,740,643
Other animal fats, lbs.	3,647,573	2,101,764	2,255,668
Australia	2,445,510	1,247,822	1,350,311
China	124,181	843,865	.....
Olein, lbs.	971,335	864,378	1,565,142
Australia	971,324	700,160	1,002,642
Stearin, lbs.	721,532	603,657	246,486
United States	.....	391,330	87,114
United Kingdom	263,848	147,010	37,438
Australia	.....	58,796	117,282
Soap:			
Perfumed, lbs.	377,576	103,940	1,235,548
United States	111,776	53,466	57,842
United Kingdom	78,377	39,577	59,635
Germany	113,400	3	.....
Other, lbs.	1,380,355	160,885	14,697
France	1,110,041	92,749	3,295
United Kingdom	115,014	45,743	37,039
United States	60,967	14,752	9,998
Oils, fats and waxes, perfumed, lbs.	58,576	42,064	20,631
France	45,809	32,524	8,792
United Kingdom	5,784	7,099	3,732
United States	831	2,180	7,659
Germany	6,023	.....	.....
Volatile oils, lbs.	285,956	426,310	673,832
United Kingdom	64,177	113,474	179,315
China	39,338	77,440	73,623
Dutch East Indies	106	67,493	170,783
France	34,905	52,828	42,748
British India	12,433	48,487	90,642
United States	108	35,220	93,923
Germany	120,735	.....	.....
All other oils, fats, and waxes, and manufactures thereof	$113,569	$221,810	$471,824
GUMS, RESINS, ETC.:			
India rubber and gutta percha, crude, lbs.	2,660,702	8,327,903	16,231,322
Straits Settlements	1,644,139	6,136,580	15,127,412
British India	337,647	1,603,330	522,001
United Kingdom	437,311	344,575	147,476
United States	138,518	122,325	93,717
Germany	15,343	.....	.....
Rosin, lbs.	15,648,616	26,082,035	26,141,718
United States	11,108,305	24,404,825	21,805,808
China	416,106	1,407,937	4,217,514
Straits Settlements	.....	141,140	30,497
United Kingdom	723,815	126,494	10,925
Germany	3,378,866	.....	.....
Shellac, lbs.	452,607	1,172,053	2,236,891
British India	450,964	1,168,470	2,202,859
Other gums and resins, lbs.	(1)	1,068,210	1,952,086
Straits Settlements	.....	440,780	542,719
Dutch East Indies	.....	236,162	702,301
China	.....	169,978	74,181
Gelatin, lbs.	118,782	26,568	98,836
United Kingdom	27,717	19,643	68,427
United States	17	4,990	23,079
Germany	82,033	.....	.....
Glue, lbs.	3,014,168	892,370	881,891
United Kingdom	547,149	466,297	37,923
France	73,690	187,353	31,262
United States	1,329	107,802	462,018
Switzerland	13,779	46,214	.....
Italy	.....	44,798	.....
Germany	1,045,307	.....	.....
Gum arabic, lbs.	615,273	359,575	309,924
British India	55,443	187,729	247,819
United Kingdom	77,393	82,095	.....
Germany	144,463	.....	.....
Pitch and asphalt, lbs.	1,053,884	1,448,712	1,971,064
United States	637,983	1,312,971	1,450,960
United Kingdom	219,273	115,333	210,644
Germany	190,383	20,408	318,460
ORES, ETC.:			
Antimony ore, lbs.	(2)	8,739,828	(2)
China	.....	8,542,735	.....
French Indo-China	.....	197,093	.....
Iron ore, lbs.	617,837,109	655,327,868	795,715,024
China	613,393,915	652,695,417	792,997,387
Lead ore, lbs.	(2)	50,120,413	7,926,188
China	.....	30,684,110	880,967
Asiatic Russia	.....	11,561,040	1,729,261
Kwangtung Province	.....	3,360,374	2,116
Russia	.....	3,360,110	.....

[1] Not given in 1913.

[2] Not shown separately.

JAPANESE IMPORTS OF CHEMICALS AND CHEMICAL PRODUCTS (*Concluded*)

ORES, ETC. (*Concluded*)	1913	1917	1918
Zinc ore, lbs.	(1)	205,807,535	132,038,936
Australia	.....	151,356,625	98,955,854
French Indo-China	.....	38,362,942	29,578,527
Asiatic Russia	.....	9,067,347	2,968,038
Other ores	$134,450[2]	$2,154,763	$2,702,522
French Indo-China	.....	215,285	112,068
Clay, lbs.	(1)	41,997,480	9,792,176
China	.....	21,270,040	1,701,382
Kwangtung Province	.....	19,930,385	6,890,854
United States	.....	671,156	285,088
Cryolite, lbs.	(1)	44,342	63,682
Sweden	.....	22,046	.....
Denmark	.....	22,046	.....
United States	.....	250	.....
Gypsum, lbs.	3,458,124	11,449,284	10,448,743
China	1,906,732	7,711,200	10,447,743
United States	.....	2,835,550	.....
United Kingdom	.....	902,490	.....
Phosphorite, lbs.	730,364,000	197,472,700	342,700,600
Australia	.....	132	324,364,900
United States	85,924,700	.....	.....
United Kingdom	48,859,600	.....	.....
Egypt	65,578,100	.....	8,640,700
MISCELLANEOUS MANUFACTURES:			
Glass and glassware	$1,696,758	$1,261,233	$1,223,614
Explosives:			
Dynamite, lbs.	2,145,280	1,415,873	2,638,856
United States	.....	1,000,966	1,874,683
Canada	.....	409,607	759,213
China	.....	.....	4,960
United Kingdom	520,757	5,300	.....
Germany	1,612,022	.....	.....
Detonators, lbs.	69,684	.....	.....
Germany	54,152	.....	.....
United Kingdom	15,532	.....	.....
Other explosives	$47,329	$11,879	$7,209
Paper	$3,604,262	$2,035,693	$4,678,954
United Kingdom	1,073,164	608,009	458,074
Germany	1,267,540	7,328	.....
Belgium	232,247	.....	.....
Austria-Hungary	177,006	3,200	.....
Sweden	506,692	256,371	58,981
Norway	99,234	111,338	86,697
United States	146,098	993,454	4,011,609
Photographic films, sensitized, lbs.	36,768	65,644	71,805
United States	21,949	53,556	59,599
United Kingdom	9,414	12,088	12,082
France	3,216	.....	8
Germany	2,124	.....	.....
Sugar:			
Under No. 21 Dutch standard, lbs.	708,149,914	174,011,370	462,418,829
Dutch East Indies	618,094,310	121,706,660	378,514,386
Philippines	82,017,770	45,245,464	76,629,983
Other, lbs.	3,051,903	68,784	30,365,454
Rock candy, cube, loaf and similar, lbs.	187,486	11,992	2,062
Grape sugar, malt sugar, molasses and the like, lbs.	2,024,528	91,966	477,849

[1] Not shown separately.

[2] Other than iron ore.

STATISTICS OF EXPORTS

The following table of exports has been compiled from the annual returns of the Japanese Department of Finance:

JAPANESE EXPORTS OF CHEMICALS AND CHEMICAL PRODUCTS

	1913	1917	1918
CHEMICALS, DRUGS, ETC.:			
Acids:			
Acetic, lbs.	(1)	5,632,007	4,663,924
Straits Settlements	.....	3,759,263	2,342,510
Dutch East Indies	.....	1,120,300	1,282,508
British India	.....	617,271	803,672
Sulfuric, lbs.	3,368,497	9,192,039	7,754,090
Straits Settlements	208,381	3,077,489	1,051,865
China	1,482,166	1,620,324	1,266,329
Egypt	.....	1,136,716	2,463,983
Asiatic Russia	315,545	1,114,249	2,534
Hongkong	409,813	773,395	1,238,424
Bleaching powder, lbs.	2,235,591	14,261,615	10,904,580
British India	132	8,384,777	6,199,441
China	1,828,436	3,926,623	2,805,811
Calcium carbide, lbs.	(1)	7,198,619	28,616,157
Australia	.....	3,855,964	10,334,972
China	.....	737,185	1,179,797
Hongkong	.....	641,717	2,072,626
Straits Settlements	.....	540,803	2,743,357
British India	.....	523,327	6,558,946
Camphor, lbs.	3,278,200	4,126,928	2,333,652
United States	659,647	1,975,073	787,873
British India	1,164,835	1,431,885	477,758
Coal tar and pitch, lbs.	(1)	27,079,515	19,394,700
French Indo-China	.....	18,356,922	7,612,252
Hongkong	.....	1,408,154	7,159,709
Copper sulfate, lbs.	(1)	3,726,754	3,454,618
Australia	.....	1,678,503	1,913,053
British India	.....	711,978	316,000
Dutch East Indies	.....	402,068	491,692
China	.....	400,361	144,900

[1] Not shown separately.

Japanese Exports of Chemicals and Chemical Products (*Continued*)

Chemicals, Drugs, Etc (*Concluded*)	1913	1917	1918
Dried plants for insecticides, lbs	346,458	3,304,297	3,197,320
United States	30,492	2,370,259	2,700,376
United Kingdom	183,465	612,469	412,073
Canada	.....	298,571	23,600
Fertilizers:			
Artificial, lbs	330,459	11,808,924	1,836,671
Dutch East Indies	.....	5,824,831	1,595,926
Asiatic Russia	.....	4,485,920	.....
Straits Settlements	153,873	79,895	.....
Phosphatic, lbs	41,306,486	43,892,522	14,945,750
Dutch East Indies	.....	16,065,736	5,236,197
New Zealand	.....	8,483,605	.....
Straits Settlements	94,380	6,521,932	1,937,995
Asiatic Russia	.....	4,989,235	.....
British India	312,448	3,711,436	.....
Cape Colony and Natal	.....	784,272	6,998,395
Australia	27,742,507	132	.....
Oil cake, lbs	(1)	2,512,343	1,749,499
Dutch East Indies	.....	61,641	1,538,253
United States	.....	1,182,295	.....
Ginseng, lbs	331,039	350,383	277,687
China	178,669	185,944	194,117
Hongkong	151,325	163,913	83,021
Insect powder, lbs	209,340	666,576	808,594
China	76,473	180,143	205,046
Australia	143	117,769	162,626
Kwangtung Province	27,818	80,435	55,965
Asiatic Russia	9,665	72,710	15,062
United States	15,902	47,776	119,991
Argentina	.....	36,613	25,368
United Kingdom	.....	20,618	63,886
Iodine, lbs	26,733	62,660	81,204
United States	.....	26,758	23,629
United Kingdom	11,393	15,042	29,843
Kaki and other tanning materials, lbs.	(1)	3,299,658	591,580
Asiatic Russia	.....	2,600,739	1,177
China	.....	637,157	393,143
United Kingdom	.....	.....	75,134
Menthol:			
Cane, doz	100,681	195,137	269,052
Dutch East Indies	26,545	66,858	76,277
China	50,523	57,891	103,129
Hongkong	14,232	30,540	43,561
Straits Settlements	2,487	19,028	12,781
Crystals, lbs	308,089	332,293	313,908
United States	54,843	196,503	99,687
United Kingdom	83,918	83,163	155,954
Naphthalene, lbs	(1)	1,394,290	1,463,838
China	.....	566,262	627,030
British India	.....	328,837	161,954
Dutch East Indies	.....	191,708	56,400
Australia	.....	67,213	416,840
Potash:			
Chlorate, lbs	(1)	3,415,669	4,772,690
United States	.....	1,617,233	228,485
China	.....	913,718	1,301,727
Brazil	.....	.....	1,228,860
Iodide, lbs	71,727	218,790	244,643
United Kingdom	63,474	86,930	36,559
United States	.....	38,294	72,303
Asiatic Russia	.....	33,373	13,786
British India	417	14,420	32,399
Soda, caustic, lbs	(1)	881,031	1,455,815
British India	.....	655,917	11,487
China	.....	145,621	195,747
Dutch East Indies	.....	2,210	810,775
Sulfur, lbs	119,613,792	188,375,054	119,263,386
Australia	53,782,290	109,692,364	79,247,950
British India	2,343,702	23,697,560	19,045,363
Cape Colony and Natal	.....	15,388,857	5,072,301
Dutch East Indies	642,681	14,766,798	5,172,619
Asiatic Russia	32,506	8,144,242	4,876
New Zealand	.....	5,523,743	1,729,720
Toilet powders	$58,727	$141,614	$176,641
China	36,477	79,207	82,311
Other prepared perfumes	$105,628	$139,064	$218,488
China	59,279	46,955	63,123
Tooth powder, paste	$119,286	$212,857	$330,176
China	82,155	132,165	182,719
Prepared medicines	$828,121	$799,723	$953,828
China	528,516	406,528	487,783
Kwangtung Province	64,848	97,948	106,305
British India	16,741	70,385	92,612
All other drugs, chemicals and medicines	$413,177	$4,596,798	$6,173,595
United States	5,448	1,098,776	976,429
Dutch East Indies	8,329	999,230	777,445
China	183,116	776,769	1,289,023
Asiatic Russia	5,730	457,413	233,917
British India	19,755	391,889	353,632
Germany	6,620	.....	.....
Argentina	508	46	456,162
United Kingdom	13,940	135,606	442,033
Dyes, Paints, Etc.:			
Paints, lbs	474,708	2,420,850	15,034,236
Kwangtung Province	435,107	758,763	1,179,955
China	35,765	567,675	1,541,667
Straits Settlements	.....	308,324	1,795,357
British India	.....	284,697	8,010,602
Dutch East Indies	.....	235,797	1,696,666
Red lead, lbs	(1)	1,895,086	4,596,276
British India	.....	1,391,191	3,059,014

[1] Not shown separately.

Japanese Exports of Chemicals and Chemical Products (*Continued*)

	1913	1917	1918
Dyes, Paints, Etc. (*Concluded*)			
All other dyes, pigments, coatings and filling matters	$150,907	$712,706	$1,752,643
China	74,990	245,316	819,552
United States	2,220	110,636	13,878
Asiatic Russia	3,501	91,668	43,974
Kwangtung Province	32,224	85,245	193,908
British India	10,253	63,498	237,700
Dutch East Indies	534	39,771	181,561
Inks, lbs	509,019	1,088,601	1,392,150
China	281,649	368,730	442,109
Hongkong	129,026	193,737	188,572
British India	3,069	133,015	236,373
Dutch East Indies	1,320	98,406	143,650
Oils, Fats, Waxes, and Manufactures thereof:			
Oil-bearing materials:			
Linseed, lbs	(1)	11,279,488	4,322,980
Peanuts, lbs	13,070,157	18,627,100	18,705,620
Rape and mustard, lbs.	(1)	13,253,105	2,721,652
Soybeans, lbs	(1)	3,379,985	1,594,854
Vegetable oils:			
Camphor oil, lbs	2,594,590	2,266,742	1,813,344
United States	1,623,410	1,687,055	1,048,932
Coconut oil, lbs	(1)	34,639,635	53,522,777
United States	.....	24,742,022	48,854,624
United Kingdom	.....	2,914,270	75
Asiatic Russia	.....	2,878,511	1,308,784
Canada	.....	1,518,996	1,681,681
Colza oil, lbs	11,664,630	19,521,925	26,620,762
United States	314,310	12,279,266	22,585,710
United Kingdom	5,711,063	4,748,987	181,133
Cottonseed oil, lbs	(1)	1,599,957	2,427,019
United States	.....	1,353,868	1,179,792
Peppermint oil, lbs	373,173	343,548	283,912
United Kingdom	118,663	185,585	193,969
United States	11,210	55,840	8,302
France	58,490	41,601	1,377
Hongkong	45,043	29,758	23,963
Soybean oil, lbs	1,879,682	7,307,968	6,518,898
United States	658,382	6,946,348	5,085,155
Vegetable wax, lbs	6,261,004	6,582,226	11,804,465
United Kingdom	972,884	2,690,668	6,050,266
United States	1,244,983	2,320,502	3,782,461
France	1,004,590	523,087	1,167,228
British India	271,490	317,333	282,487
Mineral oils:			
Kerosene, gal	(1)	3,594,024	1,655,878
China	.....	2,438,082	841,669
Kwantung Province	.....	1,151,189	658,926
Other mineral oils, lbs.	(1)	14,592,340	14,521,094
Kwangtung Province	.....	7,873,458	8,472,919
China	.....	5,950,480	3,131,906
Fish and whale oil	54,023,876	31,955,843	31,382,184
United States	246,350	15,470,291	16,173,741
United Kingdom	12,706,558	12,480,904	9,005,762
Soap:			
Toilet, doz	2,342,606	5,040,409	4,732,659
Hongkong	92,125	735,491	397,461
Kwantung Prov	228,164	414,351	524,585
British India	72,198	281,804	183,059
China	1,930,129	3,365,235	3,074,647
Dutch East Indies	1,469	162,855	374,886
United States	22	11,116	1,008
Washing, lbs	261,010	576,558	1,913,943
China	194,125	175,860	959,434
Kwangtung Prov	13,407	111,172	170,790
Hongkong	7,446	80,390	272,695
Dutch East Indies	.....	6,197	366,297
Toilet water and hair oil	$258,474	$496,036	$579,060
Dutch East Indies	49,263	148,116	187,220
China	70,002	88,319	119,523
Straits Settlements	41,908	54,606	72,938
All other oils, fats, and waxes, and manufactures thereof	$179,583	$1,116,532	$2,297,789
United States	7,892	363,906	441,808
China	27,673	248,102	392,837
Kwangtung Province	70,374	118,943	203,570
United Kingdom	11,014	111,876	178,463
Asiatic Russia	635	95,207	24,265
Dutch East Indies	114	98,416	366,205
Ores, Etc.:			
Manganese ore, lbs	(1)	12,179,700	5,188,447
United Kingdom	.....	5,721,524	1,207,957
United States	.....	5,208,288	1,392,748
Tungsten ore, lbs	(1)	1,586,534	2,644,092
United States	.....	1,379,124	2,644,092
Zinc ore, lbs	60,366,044	381,576	11,244
United Kingdom	270,770	381,576	11,244
Other ores	$680	$380,116	$244,573
United States	3	192,839	178,294
Asiatic Russia	.....	89,556	50
Antimony, lbs	3,533,080	31,466,564	6,038,036
United States	1,210,945	18,786,698	2,943,786
United Kingdom	1,810,525	10,000,745	1,669,054
Plumbago, lbs	(1)	5,608,570	4,442,308
United Kingdom	.....	4,030,243	3,972,881
Zinc dust, lbs	(1)	2,178,787	1,589,460
United Kingdom	.....	1,019,122	1,228,526
United States	.....	634,303	45,760
Miscellaneous Manufactures:			
Celluloid, lbs	(1)	956,514	1,339,445
United Kingdom	.....	855,890	352,864
France	.....	58,583	915,610

[1] Not shown separately.

Japanese Exports of Chemicals and Chemical Products (*Continued*)

	1913	1917	1918
Miscellaneous Manufactures (*Continued*)			
Explosives	(1)	443,076	638,090
Kwangtung Province	.....	203,626	356,048
Asiatic Russia	.....	173,061	7,216
China	.....	62,425	110,385
Glass	$1,652,791	$6,669,672	$8,007,614
Matches:			
Safety, gross	24,300,108	31,457,573	29,621,324
British India	6,064,182	12,489,216	8,768,973
Hongkong	9,529,743	5,302,284	5,920,397
Dutch East Indies	2,273,838	3,243,224	4,315,164
Straits Settlements	2,615,230	2,364,568	2,539,625
United States	63,347	2,311,854	1,545,631
Asiatic Russia	17,859	2,211,811	15,619
China	3,397,332	1,455,912	1,781,053
Other, gross	19,709,139	12,702,438	9,846,096
China	17,184,529	8,591,817	6,168,131
British India	453,980	2,968,973	2,675,084
Kwangtung Prov.	1,921,302	1,105,276	979,460
Metal powders, lbs.	(1)	834,382	551,092
China	.....	145,596	108,413
France	.....	138,285	24,719
United Kingdom	.....	128,548	87,430
United States	.....	110,537	9,593
British India	.....	61,986	91,794
Paper:			
"European"	$943,381	$7,038,377	$12,481,933
China	471,928	2,819,543	4,186,413
Kwangtung Province	201,028	841,121	1,180,881
Hongkong	29,308	886,544	945,148
British India	64,539	1,111,541	1,869,431

[1] Not shown separately.

Japanese Exports of Chemicals and Chemical Products (*Concluded*)

	1913	1917	1918
Miscellaneous Manufactures (*Concluded*)			
Straits Settlements	9,184	166,469	513,291
Dutch East Indies	773	458,166	1,631,012
Asiatic Russia	9,147	128,709	436,259
Philippine Islands	5,674	252,552	400,378
Egypt	14	56,530	236,540
Australia	24,305	160,787	490,295
United States	70,255	37,044	68,844
Japanese:	$598,604	$977,090	$1,695,530
China	195,790	344,990	582,424
Kwangtung Province	62,200	117,580	217,951
Hongkong	8,251	42,555	70,763
Dutch East Indies	4,569	36,943	218,109
United Kingdom	111,357	82,870	86,977
United States	127,400	246,554	194,839
Shoe polishes, lbs.	(1)	373,796	481,378
Asiatic Russia	.....	124,044	89,934
China	.....	113,852	88,332
Kwangtung Province	.....	50,136	73,938
Straits Settlements	.....	41,323	3,315
Dutch East Indies	.....	18,647	177,622
Soy, gal.	1,529,444	1,868,143	844,861
United States	539,932	764,530	123,199
Hawaii	349,820	395,627	134,312
Sugar:			
Refined, lbs.	223,240,395	292,205,874	252,488,563
China	202,051,400	197,065,352	211,632,629
Kwangtung Prov.	16,173,920	44,253,340	31,725,978
Rock candy, lbs.	94,492	4,975,830	6,698,942

[1] Not shown separately.

ORIGINAL PAPERS

THE COMMERCIAL OXIDATION OF AMMONIA

By George Arthur Perley

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Received September 4, 1919

(*Concluded from January issue*)

PURITY OF GAS MIXTURES—To review the previous pages, it may be said that the early work in the United States upon the oxidation of ammonia had developed a better understanding of the requirements of a gauze catalyst as far as the general effects of temperature, oxygen, and contact surface were concerned. A nonconducting converter and a cylindrical multi-layer catalyst had been produced which gave as satisfactory results upon a high-grade coke oven ammonia gas as did the electrically heated single-layer gauze catalyst. It was realized that one pound of nitric acid (as anhydrous) could be produced in the form of 50 per cent nitric acid at the following costs:

For electrical heat at $0.004 per k. w. h. with a single gauze	$0.00071 per lb.
For loss of platinum, by dusting of sprouts	$0.00031 per lb.

but for an average large oxidation plant, complete charges per lb. HNO_3 (100 per cent) are

Power	$0.0013 per lb.
Operating labor	0.0011 per lb.
Repairs, labor	0.00036 per lb.

and an increase of 1 per cent in conversion of 10 per cent ammonia only decreases the cost of the resultant nitric acid by $0.0003 per lb.

After making such comparisons, attempts were made to eliminate electrical heating for all types of ammonia and to increase the capacity of a given weight of platinum. Offhand, there was no available information which would indicate why one common type of catalyst could not be applied to the general ammonia oxidation reaction for ammonia from all sources.

The first attempts to apply the new ideas to the oxidation of cyanamide ammonia resulted in a sad failure. When the multi-layer cylindrical gauze was employed in the oxidation of normal autoclave cyanamide gas it was found that the catalyst rapidly developed inactive dark spots. The only means of maintaining the gauze in the active state was by operating at a ridiculously low capacity. Even under these conditions the gauze finally became inactive.

The first government experimental data upon this problem were secured at the Warners, N. J., plant of the American Cyanamid Company.

Such an exhibition was most startling to those who had seen the success of a similar converter when operating upon a high-grade coke oven ammonia. This was the beginning of the realization of the importance of the factor known as "catalyst poisons." Since this particular observation the writer has noted[1] that German Patent 276,720 covers a process of purifying ammonia as produced from cyanamide by means of sodium hydroxide solution. It was then noted that the platinum became brittle and could be used only for a short time. The presence of silicon hydride, phosphine, and acetylene was considered the cause of the trouble. These were removed by a caustic scrubber.

It should be noted that at the time when the test upon the multi-layer cylindrical gauze was made at the Warners, N. J., plant in March 1918, there were three electrically heated single-layer gauze catalysts in operation. The converters were of the so-called Landis type. A careful examination of the action of the single-layer electrically heated gauze was simultaneously made. It was noted that at periodic intervals this type of converter would also develop dark inactive spots even when heated electrically, but that the externally applied source of heat tended to stabilize the gauze action. The multi-layer nonheated gauze lacked such a stabilizer. An examination as to the oxidation conversions which were being secured on the electrically heated type of gauze was distinctly interesting in view of what has been published along these lines. Table 6 gives the data secured upon the American Cyanamid Company converters.

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[1] *Chem.-Ztg.*, **848** (1915).

TABLE 6

SOURCE OF NH_3—Normal autoclave cyanamide ammonia

DATE—Week of Marcb 1 to 8, 1918

GAUZE TEMPERATURE—As corrected for optical measurements, always between 790° C. to 870° C.

SIZE OF GAUZE—13 in. × 27 in.; exposed surface 12 in. × 24 in., Landis type

Total Cu. Ft. Gas per Min.	Vol. NH_3 Per cent	Wt. NH_3 Per cent	Lbs. NH_3 per Oz. Pt per Day	Efficiency Per cent
40–46	9.61	5.98	53.6	79.7
40–46	9.65	5.99	53.9	84.5
40–46	9.56	5.92	53.4	87.5
40–46	8.64	5.34	48.5	81.9
40–46	8.68	5.35	48.5	84.8
40–46	8.66	5.34	48.5	84.0
40–46	9.74	6.03	54.4	65.2
40–46	9.71	6.02	54.3	67.0
40–46	9.66	6.00	53.9	85 2
40–46	10.87	6.79	60.6	82.9
40–46	10.98	6.86	61.4	83.3
40–46	9.70	6.02	54.2	87.8
40–46	9.84	6.11	55.0	86.4
40–46	9.80	6.09	54.7	83.4
40–46	8.86	5.48	49.5	79.3
40–46	9.48	5.89	53.0	79.9
40–46	9.40	5.83	52.5	78.2
40–46	8.82	5.46	49.6	78.3
40–46	9.80	6.09	54.7	80.1

The above tests were made on two different converters. This same state of erratic results existed for the several succeeding weeks. Such a state of affairs had not been disclosed by previous workers.

A commercial type of ammonia gas existed which caused a serious drop in the oxidation efficiencies of a single electrically heated platinum gauze and which destroyed the catalytic activity of a nonheated platinum multi-layer gauze. An examination of a platinum gauze which had been used in the oxidation of normal autoclave cyanamide ammonia disclosed a very marked contrast to a similar gauze which had served only on high-grade coke oven ammonia. A gauze which has been used in the oxidation of a high grade of coke oven ammonia exhibits a uniformly gray sprouted upper surface. The platinum which has served in the oxidation of cyanamide ammonia presents a multiplicity of shining or sparkling masses all over the sprouted surfaces. These observations as to the relative differences were made for the first time on February 28, 1918, when the first tests of the multi-layer type of converter upon cyanamide ammonia were made. A microscopic examination of the two different types of gauze disclosed the fact that the sparkling masses on the gauze surface first appeared in the form of long crystal-like formations, and that these developed into a sort of skin over the sprouts. The preliminary examination indicated a sort of sintering of the platinum sprouts first formed.

Such observations as the above clearly indicated the necessity of rigidly defining the composition of the ammonia gas which was to be subject to oxidation. It must be noted that the cyanamide ammonia which was being produced at this period was the result of an abnormal war-time overproduction. Poor grades, as well as high, of lime nitrogen were used in the autoclaves, and it is recognized that the tests were made at an unusual period. Nevertheless, the facts were established, and another apparently very important variable had been discovered. Were there constituents in ammonia gas from other sources, such as the coke oven aqua, which accounted for the occasional inconsistencies?

A test with the same multi-layer platinum gauze which failed to function on cyanamide ammonia was made in a similar type of converter upon NH_3 from high-grade coke oven aqua on April 25 to May 18, 1918. The previously mentioned article by Dr. C. L. Parsons has given these particular data in full. It was evident that the same multi-layer gauze and type of converter which failed entirely on cyanamide ammonia yielded an average commercial oxidation conversion of 90.7 per cent at a capacity of approximately 70 lbs. of NH_3 oxidized per oz. of platinum per day at about 780° C. to 850° C. catalyst temperature.

The interesting feature of the comparison test upon coke oven aqua ammonia arose from the observation that a pure platinum gauze, which had been rendered quite inactive upon cyanamide gas, recovered its full capacity and efficiency of conversion, on a commercial scale, within a short time after operating on NH_3 produced from high-grade coke oven aqua.

PHOSPHINE INFLUENCE—Many hasty investigations were begun by several parties in an examination of the possible gas constituents of cyanamide ammonia or their effects. At this time there was practically no information available as to the nature of impurities in either cyanamide ammonia gas or in ammonia-air mixtures, as produced from poor grades of coke oven aqua.

The investigators of the Nitrate Division were misled for a short time by the presence of excessive amounts of acetylene within the normal autoclave cyanamide ammonia gas. The erroneous conclusions were soon checked. It was found possible to add acetylene from a cylinder to the ammonia-air-gas mixture without causing any serious disturbance, other than an increased temperature, upon the multi-layer nonheated gauze. This increase in the gauze temperature was a very logical effect after a consideration of the great calorific value of acetylene. Rather good evidence indicated that the troublesome constituent in the cyanamide ammonia was some form of a phosphorus compound. Whether the particular catalyst poison was phosphine has not as yet been definitely established. Lieut. C. F. Brush, Jr., was transferred from the cyanamide ammonia oxidation plant to the coke oven ammonia oxidation plant in order to work on the effect of adding phosphorus compounds to the gas entering the commercial sized cylindrical multi-layer converter which was operating on coke oven ammonia. The commercial data secured by Lieutenant Brush from June 19 to 23, 1918, while using a cylindrical multi-layer gauze, and adding varying amounts of phosphine, may be summarized in Table 7. It was observed that platinum which had been poisoned by the phosphine could be brought back to its normal operation and physical conditions within a short time. This depended upon the degree it had been poisoned and the temperature of the gauze during the succeeding oxidation with the coke oven ammonia. A laboratory series of experiments along these lines was also made by G. B. Taylor and J. H. Capps, of the Bureau of Mines, and their data were published at a later date.[1] It should be noted that the phosphine which was used in the commercial studies by Lieutenant Brush was carefully prepared by him from C. P. chemicals.

TABLE 7

TYPE OF CONVERTER—Cylindrical 9 in. × 12 in. multi-layer (4) gauze in continuous operation

PHOSPHINE CONTENT—The absolute PH_3 content cannot be guaranteed, but the figures are very close approximations

SOURCE OF NH_3—High-grade coke oven aqua

DATE 1918		Total Cu. Ft. Gas per Min.	Approx. Lbs. NH_3 per Oz. Pt per Day	Vol. NH_3 Per cent	P. p. m. of PH_3	Oxidation Efficiency Per cent
June 10		204	78.8	10.30	None	92.6[1]
		203	76.1	10.14	None	94.1[1]
June 11		203	75.7	10.11	None	93.4[1]
		200	80.2	10.70	None	93.6[1]
June 14		201	72.8	9.67	None	97.9[1]
		201	79.5	10.60	None	90.8
		201	80.2	10.70	None	90.4
June 15		200	73.2	9.70	None	90.5[1]
June 19	(2:20 P.M.)	Began adding phosphine				
	(4:20 P.M.)	200	73.5	9.81	1 in 10,000,000	59.1[1]
June 20	(11:45 A.M.)	200	80.2	10.71	None	94 6[1]
	(2:30 P.M.)	Began adding phosphine				
	(2:45 P.M.)	200	76.5	10.20	1 in 10,000,000	58.5[1]
	(4:15 P.M.)	200	76.5	10.17	1 in 10,000,000	57.7[1]
	(6:00 P.M.)	Phosphine shut off				
	(6:10 P.M.)	200	78.4	10.45	None	86.3[1]
June 22	(12:40 P.M.)	200	76.1	10.33	None	90.5[1]
	(1:00 P.M.)	Began adding phosphine				
	(3:12 P.M.)	200	76.1	10.33	1 in 50,000,000	77.4[1]

[1] Refers to an average of two simultaneous determinations.

Qualitative tests showed that when one part PH_3 per million of mix was used large inactive areas were formed. No inactive spots were formed in the above use of one part of PH_3 in ten million of mix.

However, after a gauze had been subjected to one part of PH_3 per million of mix, the subsequent addition of one part of PH_3 per ten million of mix caused the formation of inactive spots. This certainly indicated the quantitative action of the phosphine poison and showed the limitation to the use of such a type of catalyst for a normal autoclave cyanamide gas which varies in the total phosphorus content from hour to hour. For instance, the first few minutes of supply of ammonia produced by an autoclave steaming must contain the larger bulk of acetylene and phosphine (approximately 90 per cent).

The influence of the addition of small traces of phosphine upon the commercial oxidation of ammonia as obtained from coke oven aqua was most conclusive.

Although no absolutely ultimate analysis could be secured upon the cyanamide gas, it was known that the NH_3 gas leaving the cyanamide autoclaves contained distinct amounts of acetylene, phosphorus compounds (some of which reacted completely like phosphine), complex sulfur compounds, etc. To say the least, the normal cyanamide ammonia gas was a complex mixture, but the amounts of these impurities were exceedingly small. A more or less elaborate study of the situation was then begun by the members of the technical staff of the American Cyanamid Company. Simple commercial methods were developed for decreasing the content of phosphorus compounds within the cyanamide gas mixture. The test at U. S. Nitrate Plant No. 2, which has been mentioned in the article by Dr. Landis,[1] was fortunately conducted after certain of the above improvements in the autoclave operations had been made. The average 10 per cent ammonia-air mixture from the autoclave ammonia, as operated prior to June 1918, was generated from an ammonia gas containing from 50 to 100 parts of total phosphorus, expressed as phosphine, per million parts of ammonia. Reports indicate that this same ammonia probably contained from 30 to 80 parts of combined sulfur, as sulfur, per million of NH_3, and from 0.3 to 0.5 per cent of acetylene by volume. The improvements as made with the U. S. Nitrate Plant No. 2 installation in autoclave operation decreased the total phosphorus to from 2 to 8 parts of phosphorus, as phosphine, per million. This is certainly a distinct decrease, particularly as applied to a 10 per cent NH_3 mixture.

It is also most interesting to note that at a later date U. S. Patent 1,296,820 was granted to Dr. Landis, covering the blowing of air, or other inert gas, through a slurry of water and lime nitrogen to remove such impurities as acetylene and phosphine.

The records of the operations on the oxidation of normal cyanamide ammonia from February 1918 to June 1918 established facts which have been exceedingly helpful in advancing the general knowledge in the field of ammonia oxidation as a whole, and particularly as applied to cyanamide ammonia. There is still a great deal of interesting research that can be conducted along these lines. Even to-day no method has been established for quantitatively separating and determining the various small amounts of impurities within the cyanamide ammonia gas. As a result, a synthetic method of study was adopted for determining the influence of each separate constituent of cyanamide ammonia. Experimental data have been secured by other investigators in this field upon a gas mixture which had been subjected to a partial purification through the intermediate stage of the production of aqua ammonia. When an ammonia-air-gas mixture is produced from this so-called cyanamide aqua it is reported to eliminate only about 50 to 75 per cent of the total phosphorus. The relative distribution of the various phosphorus compounds has not been determined. As no method has been developed for distinguishing the amount of phosphorus present as phosphine and that present in complex ammoniacal or organic combinations, it is most dangerous to draw too rigid conclusions as to the meaning of such tests, or the action of a platinum gauze in the presence of such compounds. Up to the present time only the total phosphorus has been determined in the ammonia-gas mixtures. The facts have shown that exceedingly small amounts of phosphine exert a distinct poisonous action upon the platinum catalyst. Whether all phosphorus compounds react in the same manner is still an unsolved problem.

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[1] THIS JOURNAL, **10** (1918), 459; **11** (1919), 27.

[1] *Chem. & Met. Eng.*, **20** (1919), 476.

Investigations were being conducted upon these various problems at the time of the signing of the armistice, but these have never been completed. It may be said that practically the whole field of catalytic poisons, as applied to the oxidation of all types of commercial ammonia, still remains essentially unsolved. The incomplete investigation of the phosphine factor as carried on in the oxidation laboratories at U. S. Nitrate Plant No. 1 had indicated that phosphine in even exceedingly small amounts reacts with the surface of the platinum gauze to form possibly more than one compound. At low temperature, or from 400° C. to 575° C., there is every indication of the formation of platinum phosphide. The stability of this compound in the presence of ammonia-air mixtures is limited to a certain temperature range. The phosphide is apparently oxidized to pyrophosphate in the presence of air. By a careful control of the temperature conditions it was found possible to increase the gauze temperature to such a point as to exceed the temperature of decomposition of these compounds. A laboratory size converter was utilized in the study of the temperature-phosphine relationships. It was found possible to use ammonia-air mixtures, containing much higher quantities of phosphine than corresponds to the total phosphorus of autoclave cyanamide gas mixtures, without any apparent poisonous actions. The operations at U. S. Nitrate Plant No. 2 were discontinued just as plans were being made to test this out on a large scale. All preliminary indications pointed to the fact that certain of the phosphorus compounds within the cyanamide gas mixture reacted with the platinum to form well-established compounds. These compounds appeared to be decomposed above a certain maximum temperature. By the use of a properly adjusted platinum catalyst temperature it should be possible to prevent the formation of these compounds and thus eliminate the poisonous action. It is unfortunate that this work could not have been continued on a semi-commercial development. It seems as if the stabilizing action of the electrical heat upon a single platinum gauze is possibly a result of continually maintaining the gauze temperature above a certain minimum as demanded by the above-suggested reactions. The method of determining the exact gauze temperature for a single layer of catalyst, by means of an optical pyrometer, is unquestionably quite inaccurate. The pyrometer cannot be focused on the single wires without introducing the large error of the colder spaces between the wires. The uses of thermocouples are limited because of the activations and resultant inconstancy of such.

In view of the possibility that all grades of ammonia might have to be utilized in another period of emergency it seems as if this whole problem of poisons as applied to cyanamide gas mixtures should be thoroughly worked out. A very large amount of preliminary data upon the oxidation of cyanamide ammonia has been secured. Only a very brief synopsis of this is given above. Future investigations will meet success only after developing quantitative methods of analysis as applied to the specific problem. A complete micrographic study will also be required.

COKE OVEN AQUA IMPURITIES

Almost simultaneously with the above experience with cyanamide ammonia, it was learned that all grades of coke oven aqua did not perform well with a non-externally heated type of catalyst.

The original experimental data upon the utilization of nonelectrically heated platinum catalysts for the oxidation of ammonia had been conducted with a high grade of coke oven aqua. While the exact composition of the impurities in the so-called Grade A aqua was known to vary within certain limits, this variation apparently had involved no serious commercial troubles. A certain amount of the so-called R & H, or B, grade of aqua had been used, with apparent success, in the work by the Semet-Solvay Company. This second-grade quality of liquor was utilized in the initial operations at the oxidation unit of U. S. Nitrate Plant No. 1. Analysis of a rather high-grade R & H aqua shows it to consist of:

Per cent NH_3	29.53 per cent
H_2S	0.00 g. per liter
CO_2	0.06 g. per liter
Pyridine	0.11 g. per liter
Organic	100 cc. of liquor takes 114 cc. $N/100$ $KMnO_4$
Naphthalene	0.084 g. per liter or 0.0095 per cent
Soluble tar	0.037 per cent

This represents an exceptionally high grade of the B liquor, as the normal Grade B liquor has an organic number of more nearly 200.

In a Grade A liquor the organic matter, naphthalene, and soluble tar content is approximately 50 per cent of the above. For instance, the typical Grade A aqua shows:

NH_3	25–28 per cent
H_2S	0.00 g. per liter
CO_2	Never over 0.50 g. per liter
Pyridine	Less than 0.1 g. per liter
Organic	100 cc. of liquor must take less than 50 cc. $N/100$ $KMnO_4$
Naphthalene	Less than 0.01 g. per liter

In view of the fact that these last-mentioned differences are small, and since, at that time, the cost of Grade A liquor was 5 cents per pound of NH_3 more than a Grade B material, it was a matter of economics to utilize the Grade B liquor. It is quite clear that with this difference in the NH_3 cost of the two grades of liquor it would only be necessary to obtain a 75 per cent conversion with the B liquor to compete with a 100 per cent conversion on the A liquor.

Prior to this time, the matter of the gas composition and the distribution of the impurities of the aqua into the ammonia-air mixture had received but meager attention. It was learned that the large portion of the pyridine, naphthalene and soluble tar was removed with the ammonia when blowing air through a stripping column such as was used for the production of the ammonia-air mixtures from aqua ammonia.

However, the effect of a substance like naphthalene ($C_{10}H_8$) upon the oxygen concentration is very important when using air as the source of the oxygen, A comparison of the oxidation reactions of ammonia and naphthalene shows that the oxidation of one per cent of naphthalene by volume requires roughly the same volume of oxygen as the oxidation of 10 per cent ammonia. Since both of these reactions occur at the platinum gauze it is quite important that information be secured as to the nature of the gas mixture. It will be noted that the naphthalene content of an ammonia-air mixture produced from Grade B aqua is distinctly high, and thus greatly decreases the active oxygen concentration at the catalyst.

PREHEATED AIR DEVELOPMENT

The result secured by the use of the secondary grade of coke oven aqua at the oxidation unit of U. S. Nitrate Plant No. 1, over a period of several weeks, was considerably below the standard previously secured on the test converter at Syracuse, N. Y., when operating on somewhat better grades of aqua. The only apparent variable which had been altered from the previous commercial tests was that of gas composition. The data of Table 8, using the cylindrical four-layer nonexternally heated gauze, are typical. In all of the work after June 1918 the modified gravimetric analytical method, similar to that described by Captain Gaillard[1] was used.

Table 8

Operation—At Oxidation Unit of U. S. N. P. No. 1

Source of NH_3—Grade B coke oven ammonia (composition given above)

Date—April 4, 1919

Catalyst—Cylindrical 4-layer 0.0026 in. wire, 9 in. diameter × 10 in. high; 13.7 oz.

Analysts—Montilion, Newton, Kennedy, and Coe

Hour	Cu. Ft. Gas per Min.	Vol. NH_3 Per cent	Lbs. NH_3 per Day per Oz. Pt	Gauze Temp. Corr. (as per B. of S. Meas.)	Conversion Per cent
9.58	113	10.6	53.8	820	86.1
9.58	113	10.6	53.8	820	86.1
10.50	122	12.3	67.8	912	90.7
10.50	122	12.3	67.8	912	92.2
11.50	112	11.6	58.7	890	89.0
11.50	112	11.3	57.2	890	87.3
12.30	112	11.7	59.2	912	90.2
12.30	112	11.7	59.2	912	90.7
4.25	112	9.0	45.6	780	87.1
4.25	112	9.1	45.6	780	87.3
5.45	117	11.4	60.2	925	86.1
5.45	117	11.4	60.2	925	88.6
6.40	112	11.2	56.6	912	88.6
6.40	112	11.2	56.6	912	89.4
7.15	100	10.4	47.1	890	88.0
7.15	100	10.4	47.1	890	90.3
8.30	152	9.50	65.4	780	84.0
8.30	152	9.47	65.4	780	85.7
8.30	152	9.45	65.4	780	86.2
8.30	152	9.45	65.4	780	87.6
10.10	168	10.50	80.0	870	85.6
10.10	168	10.65	81.0	870	82.8
10.35	152	10.5	72.1	850	84.8
10.35	152	10.4	72.1	850	87.3

The temperature corrections used in all this work for the modified Morse optical pyrometer observed readings are given in the curve of Fig. 3. It must be noted that the data as secured in Table 8 represent ideal commercial operation and much care was employed in maintaining good operating conditions. A very large amount of data has been accumulated on the same converter and gauze and with a slightly poorer Grade B of aqua which gave averages nearer to 85 per cent oxidation efficiency. However, with a Grade B coke oven aqua, of an organic number around 114, the above is quite characteristic. The poisonous action, when using a multi-layer catalyst, begins to increase in activity as the organic content of the coke oven aqua increases. The variation in the gauze action was distinctly evident. Similar variations had been encountered with the electrically heated single gauze on cyanamide ammonia gas. It is not necessary to cite more data to show the limitations of a non-externally heated multi-layer gauze catalyst for the use of other than very pure NH_3. Many hundred commercial efficiency determinations have been secured upon the impure grades in an effort to solve the problem, but to no avail.

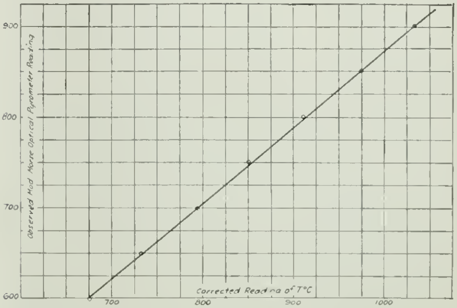

Fig. 3

The indications of all the work upon a multi-layer type of catalyst, as applied to less pure grades of NH_3, pointed to the great desirability of oxidation at the highest possible temperatures. The increased catalyst temperature apparently selectively favors the velocity of the nitrogen oxide formation reaction. In other words, when oxidizing ordinary commercial grades of ammonia the relationship between time of catalyst contact and speed of reaction is distinctly important. After a thorough realization of the vast importance of the above-mentioned factors, attempts were made to speed up the velocity of the nitrogen oxide formation reaction and thus greatly decrease the catalyst contact time.

While Dr. Landis[1] has considered "the experiments were critically reviewed and it was concluded that the hot gauze radiated heat to the oncoming ammonia-air mixture and decomposed some of the ammonia" it did not seem physically possible that the oncoming gas could be heated by radiated heat. However, the ready catalysis of ammonia-air mixtures to nitrogen by contact with hot iron tubes, etc., had been recognized. While silica tubes have but little influence upon the catalytic decomposition of ammonia-air mixtures, such a fragile and nonconducting material does not lend itself particularly well to a commercial heat exchange. Aluminum exchanger tubes would unquestionably soften or melt at the temperatures employed. From this standpoint, the use of a heat exchanger on the oncoming ammonia-air mixture seemed distinctly undesirable as a means of increasing the gauze temperature.

The two most obvious methods for increasing the temperature of the catalyst, without the use of external energy, were operation with a higher ammonia concentration, or else the use of a heat exchanger upon the oncoming air, and mixing this with the required ammonia just prior to the catalyst entrance.

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[1] *Loc. cit*

[1] *Chem. & Met. Eng.*, **20** (1919), 472.

When using air as the source of the oxygen we can consider the reaction at 800° as

$$4NH_3 + 5O_2 + 18.8\ N_2 + Pt =$$
$$4NO + 18.8\ N_2 + 6H_2O + Pt + 211{,}750\text{ g. cals.} \quad (15)$$

As applied to a 10 per cent NH_3 commercial gas mixture we have

$$10NH_3 + 2.8H_2O + 18.3O_2 + 68.9N_2 =$$
$$10NO + 17.8H_2O + 68.9N_2 + 5.8O_2 \quad (16)$$

or as applied to a 13 per cent NH_3 mixture we have

$$13NH_3 + 2.8H_2O + 17.68O_2 + 66.52N_2 =$$
$$13NO + 22.3H_2O + 66.52N_2 + 1.43O_2 \quad (17)$$

It will be seen that with a 13 per cent ammonia-air mixture, as prepared without taking precautions to dry the air mixture, the excess of oxygen is very meager. This represents the limitations to the use of high ammonia concentrations for the increase of the catalyst temperature. Such a limitation does not apply in case spillage oxygen is available.

Although it was evident that an increased ammonia concentration of the intake ammonia-air mixture would increase the gauze temperature, a maximum in the efficiency-temperature curve would result when an ammonia-air mixture which yielded insufficient excess oxygen was obtained. The typical commercial data upon 12 per cent NH_3 mixtures are given in Table 9. These data were secured on the same Grade B aqua as that of Table 8 and represent the comparison to the operation at lower catalyst temperatures.

TABLE 9

OPERATION—At Oxidation Unit of U. S. N. P. No. 1

SOURCE OF NH_3—Grade B coke oven aqua

DATE—April 8, 1919

CATALYST—Cylindrical 4-layer, 0.003 in. wire 9 in. diameter × 11 in. high; 21.5 oz.

ANALYSTS—Montillon, Newton, Kennedy, and Coe

HOUR	Cu. Ft. Gas per Min.	Vol. NH_3 Per cent	Lbs. NH_3 per Day per Oz. Pt	Gauze Temp. Corrected	Conversion Per cent
9.50	150	11.1	47.5	915	85.7
9.50	150	11.1	47.5	915	86.2
10.35	165	11.5	54.6	925	88.9
10.35	165	11.5	54.6	925	87.8
12.00	150	12.5	54.3	990	87.0
12.00	150	12.5	54.3	990	87.6
1.00	145	12.6	52.6	990	90.4
1.00	145	12.6	52.6	990	88.6
2.00	145	12.3	51.4	980	88.7
2.00	145	12.3	51.4	980	89.3
3 15	145	12.5	52.2	995	90.6
3.15	145	12.4	52.2	995	88.6
4.15	145	13.3	55.5	1030	86.9
4.15	145	13.4	55.5	1030	89.5
5.20	120	13.5	56.2	..	88.2
5.20	120	13.5	56.2	..	89.8
6.25	122	12.4	43.5	995	91.9
6.25	122	12.3	43.5	995	92.4
7.15	122	11.7	41.2	975	91.8
7.15	122	11.7	41.2	975	..
8.19	145	12.1	50.5	980	90.9
8.19	145	12.0	50.5	980	90.5
8.50	145	12.1	50.2	995	90.2
8.50	145	12.1	50.2	995	89.0
9.15	152	12.05	50.2	915	92.2
9.15	152	12.00	50.2	915	91.2

It is quite evident that there was less variation in the operation when the high ammonias and temperatures were employed. A distinct advantage results from the oxidation of high concentrations of ammonia, since a correspondingly high NO gas mixture results. The absorption of the resultant oxides becomes much more efficient. An important limiting factor to the use of any nonexternally heated multilayer type of converter lies in the lack of an adequate temperature control. Such a control as is secured by auxiliary electrical energy, or a suitable heat exchanger, is distinctly a commercial advantage. There was still such an opportunity for improvement that it was decided to operate a heat exchanger of commercial size and thus obtain the corresponding data as to the selective temperature-reaction velocity effects.

A heat exchanger was constructed at the Oxidation Unit of U. S. Nitrate Plant No. 1 out of standard 12-in. pipe and fittings which were readily available. The interchanger casing was 14.5 ft. long by 12 in. diameter and contained 19 standard 2-in. boiler tubes. The 144 sq. ft. of steel tubes did not present sufficient heat transfer surface. However, sufficient data were secured during the plant operations for the design of a proper exchanger. A by-pass is also an essential requirement.

The only available source of ammonia was in the form of Grade B coke oven liquor. The apparatus at Plant No. 1, for the production of ammonia-air mixtures from such, consisted of a countercurrent stripping column. Ammonia-air mixtures of varying NH_3 content could be produced at will, depending upon the feed of 29 per cent liquor into the top of the column, and the flow of air and temperature at the base of the same. It was realized that separate mains of air and NH_3 would be far more desirable than the above system. Future equipments should be thus installed.

An approximately 30 per cent NH_3-70 per cent air mixture was continuously generated in the ammonia column. Air was allowed to pass through the exchanger tubes, while the hot NO gases from the oxidation reaction surrounded the tubes; the air which was thus heated through proper interchange from the gases of the reaction, and the cold ammonia air were allowed to mix within a heat-insulated, 6-in. aluminum pipe just prior to the entrance to the catalyzer holder. A silica-lined iron pipe with a silica baffle plate would be preferable for this mixing chamber. Decomposition of the mixture was thus prevented. This is due to the high velocity within the line and the short period of contact of the hot ammonia-air mixture with any material prior to the gauze entrance. A general tabulation of the average data on the heat exchanger is given in Table 10.

TABLE 10

APPLIANCE	Total Cu. Ft. Gas per Min.	TEMPERATURE ° C.
Air intake to tubes	175	At 30
Heated air exit from tubes	504	At approx. 500
Hot NO mix outside tubes entering	903	800
Cooled NO mix outside tubes leaving	...	450
30 per cent NH_3-70 per cent air entering mixer	80	30
Heated 10 per cent NH_3-90 per cent air	...	300
Heated mix at cylinder entrance	...	650
Gauze	...	1025

Since the 144 sq. ft. of exchange tube surface served to cool the exit NO-H_2O gas mixture only to 450°, it is quite evident that a transfer surface of 200 sq. ft. should be provided for a converter oxidizing 1800 lbs. of NH_3 per day. It is undoubtedly safe to cool the hot gases from the temperature at which they leave the gauze to 140° C. Greater cooling than this may lead to troublesome condensation within the exchanger.

By means of a by-pass from the heat exchanger it is possible to control the temperatures of oxidation by the above modified method.

A continuous 24-hr.-per-day test was conducted upon this modified converter before its upper working capacities had been established. A total of 121 efficiency determinations were taken over the whole period of the test. A 4-layer platinum gauze of 0.003 in. diameter wire and 80 mesh, in the same type of cylindrical multi-layer converters as used on the previous-mentioned test, gave a test average of 95.1 per cent oxidation efficiency on 9.88 per cent NH_3 gas mixtures at a rate of 2.1 cu. ft. of NH_3 per min. per sq. ft. of exposed gauze surface. There were no preliminary arrangements for the above-mentioned test, since it was conducted at an unexpectedly early time due to a rapidly diminishing supply of Grade B aqua. The gauze had been in continuous service prior to the test. The 121 efficiency determinations exhibited consistent agreements and the whole plant operation was practically automatic. Since this test chanced to be carried out on an 0.003 in. diameter wire and 80-mesh gauze, with a total exposed surface in the four layers of 8.6 sq. ft. (*i. e.*, 2.3 sq. ft. per layer), only 60.0 lbs. NH_3 per oz. of platinum per day were oxidized. It does not seem necessary to give a tabulation of these 121 efficiency determinations. It is interesting to note that the first operations on the heat interchanger for the air intake utilized a platinum catalyst of four layers of 0.0025 in. diameter wire at 80 mesh. Equally as high conversions were obtained with the same rate of gas flow as when using 0.003 in. diameter wire gauze. The yield per ounce of platinum is thus considerably increased over any previously obtained in the United States.

The use of the heated gas mixture on a 10 per cent NH_3 gas increased the 4-layer cylindrical gauze catalyst temperature a total of approximately 250° C. The speed of the NO formation reaction is thus greatly accelerated, and with much less contact time of the gas molecules with the platinum surface the period for the nitrogen formation reaction is not sufficient. By decreasing the contact time of the gas with the catalyzer surface and through a proper proportioning of temperature, the time for the preferential oxidation of ammonia to the oxides of nitrogen, rather than to the ultimate nitrogen, is secured. The heat is obtained from the gases produced in the reaction, and hence no external energy is utilized. It had always been necessary to cool these gases prior to their absorption in water, hence the auxiliary hot nitric oxide to air exchanger served a double purpose. By mixing the heated air with the cold ammonia gas, or rich ammonia-air mixture, just prior to the catalyst entrance and within an aluminum, or preferably silica-lined iron pipe, no decomposition or pre-catalysis to nitrogen results.

A U. S. Patent, 987,375, by Kaiser covers the use of externally heated air in connection with this work. Dr. Landis[1] has written of the Kaiser method as follows: "The direct heating scheme used by Kaiser required the combustion of additional fuel and seemed to have no apparent advantages of any sort over the Ostwald system." The commercial developments at the Oxidation Unit of U. S. Nitrate Plant No. 1 worked up to the use of the air exchanger on the catalyst chamber step by step. The improvements over the work of Kaiser consisted not only in utilizing the exchange of heat from the hot gaseous products of the oxidation reaction, but the conditions to prevent predecomposition of the resultant hot ammonia-air mixture were established. The previous failure of the former heat exchangers have been due to the necessarily long contact of the heated ammonia-air mixture with the heat-exchanging surface. A resultant decomposition of a certain amount of the ammonia prior to its entrance to the gauze must follow

An increased gauze temperature can be secured for low ammonia concentrations by the above methods. This permits the use of sufficient oxygen, from air alone, to yield much more efficient oxidation. Not only does the higher temperature increase the velocity of the oxidation reactions, but the increased oxygen content of the lower ammonia mixtures favors the nitrogen oxide formation reaction. Thus, we observe the tremendous interdependence of oxygen, temperature, and contact surface upon the speeds of the reactions under consideration. The importance of this extra amount of oxygen is particularly great for gas mixtures containing impurities in the form of complex molecules which are easily oxidized, such as naphthalene, soluble tars, phosphine, etc.

The work mentioned above demonstrated that a high efficiency of oxidation of ammonia could be secured by the use of a multi-layer type of gauze for poorer grades of ammonia. It has been possible to oxidize a good quality of Grade B coke oven ammonia with from 88 to 89 per cent conversions, when using a 12 per cent (by vol.) NH_3 mixture at the rate of 50 lbs. of NH_3 per oz. of platinum per day. The methods were so improved at the first tests as to secure 95 to 96 per cent oxidation with a minimum capacity of 60 lbs. of NH_3 per oz. of platinum.

CAPACITY TESTS WITH AUXILIARY AIR EXCHANGER

It seemed advisable to attempt capacity tests upon the modified form of oxidation equipment. The supply of coke oven aqua at U. S. Nitrate Plant No. 1 was nearly exhausted, but the operations were sufficient to give an estimate as to the value of the improvements. Greater gas flows than given in the data of Table 11 could not be secured from the available equipment at the time of the tests. The data of Table 11 merely show that even to-day we have no information as to the upper capacity limit of the modified type of converter. The improvements are a distinct advantage as far as the conservation of platinum is concerned, for the platinum depreciation, as compared to other operating costs, is an important item in the total operating charges. Not only have high commercial oxidation efficiencies been secured, but a great saving in platinum depreciation has resulted.

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[1] *Loc. cit.*, p. 474.

TABLE 11

OPERATION—At Oxidation Unit of U. S. N. P. No. 1
SOURCE OF NH_3—Grade B coke oven aqua
DATE—May 1, 1919
CATALYST—Cylindrical 4-layer gauze with heat exchanger
ANALYSTS—Montillon, Newton, Kennedy, and Coe

HOUR	AIR	Cu. Ft. per Min. Air-NH_3 Mix.	Total	Vol. NH_3 Per cent	Gauze Temp. ° C.	Conversion Per cent
1.10	158	88	246	10.27	1005	95.5
1.15	166	89	255	9.90	995	95.5
1.25	166	90	256	10.20	1005	93.6
2.00	166	89	255	9.94	1010	94.6
2.20	166	91	257	10.33	1018	93.5
3.00	166	73	239	9.48	1025	97.5
3.30	171	79	250	10.15	1035	96.2
4.15	195	80	275	8.60	980	95.0
4.30	197	81	278	8.65	990	96.4
5.00	168	87	255	10.33	1050	94.4
5.30	171	90	261	10.31	1075	95.8

The data of Table 11 are averages of two determinations on simultaneous samples.

There was no assurance but that much greater gas flows could be oxidized. The highest capacities of Table 11 as applied to the oxidation of a Grade B coke oven ammonia by means of a 4-layer cylindrical gauze of 0.0026 in. wire and 80 mesh, show that a conversion of 95 per cent can be secured at the rate of 100 lbs. NH_3 per oz. of platinum per day, and a catalyst temperature of over 1000° C. This is essentially double the capacity and with 4 per cent higher conversions than secured on the tests of the single-layer electrically heated Landis type of converters at Plant No. 2.

As applied to the oxidation of ammonia for the 33,000 lb. NH_3 oxidation units at U. S. Nitrate Plant No. 1 it means a yearly saving of 481,800 lbs. of NH_3, provided high-grade NH_3 could be secured. Fifty per cent of the platinum requirements is also eliminated by the use of the heat exchanger. There would also have been an additional yearly saving of 5,694,000 k. w. h. alone in case the electrically heated, single-gauze type of converter had been adopted for use at U. S. Nitrate Plant No. 1. A figure for the saving on this size of plant, expressed in dollars and cents, when using the modified type of converter over the electrically heated form depends much upon the value of NH_3 and the cost of electrical energy. As a minimum, it represents a yearly operating saving of $100,000, and this can make or break the application of such a plant to ordinary commercial competition.

REQUISITES AND LIMITATIONS OF A MODERN CATALYST

An outline of the development of the processes for the oxidation of ammonia by means of the oxygen of the air has been given step by step. While this article has been unduly long it must be admitted that many rather important details have still been omitted. Success with the cylindrical multi-layer gauze type of catalyst was not obtained until methods of mounting the four layers upon the cylindrical holder had been solved. While in theory a silica cylindrical holder may seem to prevent undue decomposition, and have all the other ideal characteristics, still in practice such a form of catalyst holder is very unpractical. A nickel holder, which is shown in Figs. 4 and 5, was developed at U. S. Nitrate Plant No. 1. Prior to the use of this type of holder serious troubles were encountered from the influence of the relative expansion effects of the platinum wire gauze, the clamping wire and the cylindrical gauze holder frame. Silica cylindrical holders with either platinum wire or Invar clamps failed to satisfy the demands for making a tight connection, at all temperatures, between the gauze catalyst and holder. When using the improved double ring clamp on the nickel cylinder and base, all the failures due to the gauze mounting were eliminated. A nickel-steel cylinder, which is protected by means of a silica tube of very slightly smaller outside diameter than the inside steel cylinder diameter, will make a better and more economical gauze holder than one of pure nickel. The protecting silica tube is to be recommended for all installations utilizing a preheated ammonia-air mixture, since nickel promotes a certain amount of predecomposition.

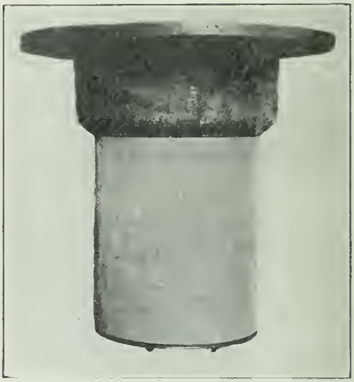

FIG. 4

While the cylindrical form of a 4-layer gauze catalyst was used in the commercial tests on heated intake mixtures with excellent success, nevertheless, the cylindrical form of platinum gauze as used to-day has certain limitations. The real feature of the gauze cylinder consists in the stability of the gauze temperature conditions which result from the radiations from the catalyst surfaces within the intake side of the platinum cylinder. This effect becomes clearly illustrated if a solid nickel cone is suspended within the inner zone of the cylinder. A series of tests was carried out at U. S. Nitrate Plant No. 1 as to the influence of various methods of gas distribution to the non-preheated cylindrical type of gauze. It was interesting to note when using a special tangential aluminum nozzle to deliver the oncoming gas, with a high velocity, tangentially to the surface of the gauze, that absolutely every trace of vibration on the gauze was eliminated. The same effect was produced when using preheated mixtures. When using the nonheated original type of cylindrical gauze catalyst, or a flat catalyst, it is very easy to observe waves and flickerings upon the gauze. The introduction of a nickel cone within the inner section of the cylinder caused a drop in the gauze temperature which could be detected by the eye. This was very obvious when a cone only half the total height of the gauze was employed. This served best to show the function of the radiations within the nonheated cylindrical gauze. Good oxidation results may be obtained upon most any form (flat, etc.) of platinum gauze catalyst on Grade A ammonia, provided it is installed within a nonconducting casing. However, the greater the uniformity of the gauze physical conditions, temperature, etc., the less the catalyst responds to occasional variations in operations.

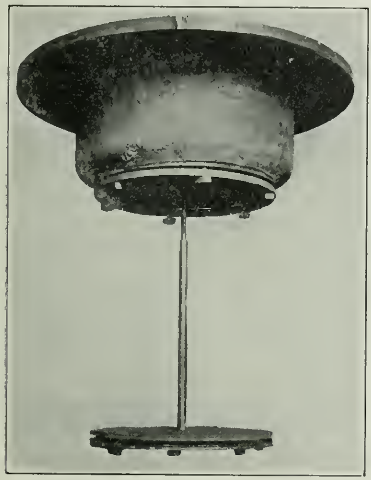

Fig. 5

The writer does not believe any catalyst can operate day in and day out with high commercial conversions without a flexible control of the catalyst temperature. This statement does not apply to C. P. ammonia-air mixtures. Yet it is more logical to oxidize commercial ammonia with a catalyst equipment which insures freedom from variations. The use of an electrically heated catalyst, or a heat exchanger of proper design, will solve the problem for the average grades of commercial ammonia. In view of the recent work it seems ridiculous to use electrical energy. As a matter of fact, the writer believes that the use of electrical energy as a means of securing gauze temperature should not be considered even if it could be secured gratis. The reasons for this opinion are based upon the conclusions derived from the series of commercial studies of the past year. The major functions of a preheated intake air mixture in the oxidation of ammonia are:

(1) The establishing of a high catalyst temperature in the presence of a distinct excess of oxygen. This means a high catalyst temperature for a low ammonia concentration.

(2) The correct proportioning of the gas velocity before and after the catalyst. The effect of a preheated gas mixture as a physical stabilizer to the catalyst is certainly an important feature. It is making enormous demands upon a gauze when a cold ammonia-air mixture is delivered to a thin layer of catalyst surface, which is heated to about 900° C. by the exothermic character of a reaction, to expect a high temperature in the gas phase and perfect gas distribution. The best results in this oxidation reaction are obtained when the temperature gradient is carefully adjusted. The preheated gas mixture should be delivered to the gauze at as high a temperature as possible and thereby decrease the otherwise abrupt volume expansion effects which are caused by the decided changes in temperature. It is the temperature of the gas phase which governs the reaction velocity.

The method of accomplishing these desirable features, without the pre-catalysis or decomposition of the ammonia prior to its entrance to the catalyst, was worked out in the commercial size units at U. S. Nitrate Plant No. 1. Nernst has studied the displacement of the equilibrium of the arc nitric oxide formation reaction along a temperature gradient. It is perhaps possible that the cooling may be in the order of 1000° per millimeter, and that the equilibrium corresponding to the temperature of each thin layer is rapidly adjusted. However, the interesting relationships were those existing between diffusion forces and reaction velocity. While the ammonia oxidation reaction may not be of the same magnitude, yet the relative effects of diffusion and reaction velocity must affect the stability conditions to a distinctly different degree, when a heated intake gas is delivered to the heated catalyst, than when a cold gas is used.

When using the cylindrical form of catalyst, it will be observed that there must be a definite ratio of diameter to height in order to secure the best gas distribution to the gauze. This is of particular importance when utilizing nonheated gas mixtures. These ratios have not as yet been well established. When using the preheated mixture the matter of distribution at the gauze does not become so important.

Unless the bottom section of the cylinder is protected with a silica cover there is an opportunity for a certain amount of decomposition. This bottom metallic plate also exerts a slight cooling effect upon the extreme edge of the gauze. In an effort to eliminate these objections the writer has made a mantle of a small platinum gauze similar to the familiar Welsbach gas mantle. A very good mantle can be formed by adjusting the height of the gauze to the diameter in such a manner as to enable the edges of one side to be doubled over and sewed together with a platinum wire. This form of platinum mantle exhibits a particularly delightful effect and there is also a distinct platinum saving over the cylindrical type. It will be very clear that in the use of a platinum mantle catalyst only one edge of a gauze is utilized in clamping it to the holder. With a flat gauze the four edges must be retained by a proper flange or clamping device. When using a 9-in. diameter cylinder with even the improved closed bottom plate and four layers of gauze, there is a protected surface of 113 sq. in. out of the total 1470 under the edges of the clamps. Thus, there is a platinum surface loss of practically 8 per cent, even when using a cylinder where only two edges of the gauze are covered with the clamps of the gauze holder. This loss is still greater in a flat installed gauze where four edges must be clamped.

The work which was conducted on a plant-size scale at U. S. Nitrate Plant No. 1 certainly has increased the working knowledge along the lines of ammonia oxidation. The general limitations of many designs of catalyzers have been determined and the relative importance of the large number of variables has been studied. The above paragraphs will serve to indicate only the more important features of the work. A form of platinum catalyst converter has been developed which will greatly excel all other present existing types, yet even this type can be excelled when an exact working theory of the true nature of the reaction has been established.

SUMMARY

I—The influence of the more important factors involved in the oxidation of ammonia have been discussed.

II—It has been shown that the coördination of catalyst temperature, gas-phase temperature, oxygen concentration and catalyst contact time must be made with great care. The interdependence of these factors, when dealing with commercial grades of ammonia, has been briefly discussed. An expression of one factor in the absence of the others is meaningless.

III—The importance of the use of some form of controlled temperature regulation for the catalyst and intake gas mixture has been demonstrated. This may be accomplished in part by means of outside electrical energy, or in whole by a proper utilization of the heat of the oxidation reaction.

IV—The use of a nonexternally heated multi-layer platinum gauze catalyst results in a decided decrease in capacity and NO conversion efficiency over that obtained when using preheated air mixtures.

V—The use of electrical energy as a source of heat for the catalyst is not only extravagant, but it also does not satisfy the demands for sufficient gas temperature and distribution to the catalyst.

VI—A single-layer gauze catalyst is distinctly impractical.

VII—A decided economy of platinum will result by using the smallest area of space between the wires (large mesh) and the smallest diameter of wire consistent with fabrication costs. An iridium alloy with platinum can be used to secure sufficient ductility and tensile strength in the finer diameter wires. It is probably impractical to employ wires of much less than 0.0026 in. diameter. A mesh of at least 120 should be employed for a single-layer catalyst. The various layers of a multi-layer catalyst should not utilize the same diameter of wire and mesh of gauze. The use of a 0.0026-in. diameter wire and 120-mesh platinum (with small amounts of iridium) gauze in the form of a gas mantle has been recommended as a desirable catalyst. The minimum economical size of wire is limited by the sprouting effect and recrystallization of the platinum during catalysis and the resultant decrease in tensile strength. The use of a heat-conducting coarse mesh separator, such as a $^1/_4$-mesh, $^1/_{16}$-in. diameter platinum gauze, enables the utilization of far greater surfaces of platinum per unit height of a multi-layer gauze catalyst.

VIII—A method of platinum gauze activation without the use of electrical energy has been outlined. The use of a separated gauze layer and a coarse mesh platinum wire separator enables the activation of a new gauze when it is placed as the second layer of a multi-layer catalyst. Any form of conducting separator between the layers can be used to good advantage provided it does not protect too large a percentage of the new gauze surface.

IX—The use of a heat exchanger on the combined ammonia-air mixtures involves serious commercial operating troubles and promotes the pre-catalysis of the ammonia to nitrogen.

X—The use of a heat exchanger, by which the heat content of the gaseous products of the oxidation reaction is transferred to the air of the intake ammonia-air mixture, has been employed in large-scale operations. An arrangement for the mixing of the heated air with the ammonia just prior to the catalyst entrance has been employed. This mixing chamber and catalyst holder on the ammonia-air side should have a silica lining.

XI—The advantages in the use of the above described heat exchanger as employed in the oxidation of ammonia consist in:

(*a*) The preheating of the intake ammonia-air mixture without the decomposition of the intake gas constituents through pre-catalysis to nitrogen.

(*b*) A sufficiently increased catalyst temperature is secured whereby it becomes only slightly affected by commercial operating variations, or periodic poisons.

(*c*) A sufficiently high temperature in the gas phase cannot be obtained with the normal high gas velocities and resultant short periods of catalyst contact even when using electrically heated catalysts. The desirable feature of the whole oxidation reaction is the production of high reaction speeds or velocities for the short period of contact. The preheating of the ammonia-air mixture accomplishes this better than any other method. The waste heat of the oxidation reaction should be employed since the gaseous products have to be cooled prior to their absorption.

(*d*) The physical instability of the gauze is reduced to a minimum by the use of preheated mixtures. The sudden volume expansion changes caused by an excessive instantaneous temperature rise are prevented by the use of preheated mixtures. The catalyst holder design should be so made as to deliver the gases to the catalyst at as nearly the catalyst temperature as possible.

(*e*) The extending of the catalyst holder proper to a decided distance within the nonconducting chamber makes it possible to utilize the maximum radiation and conduction effects. This design applies to flat as well as cylindrical gauze installations.

XII—A form of commercial catalyst has been described which will oxidize at least 100 lbs. of NH_3 per day per ounce of 0.0026-in. diameter wire and 80-mesh platinum gauze at 95 to 96 per cent conversion to NO. It is probable that the capacity is even greater than these figures.

XIII—The influence of such poisons as naphthalene, soluble tar, phosphine, etc., have been studied. The action of the above-mentioned poisons can be minimized by the use of high oxygen concentrations with simultaneous high gas and catalyst temperatures and minimum times of catalyst contact. The poisoning by phosphine is of quite a different character than that of naphthalene. It appears that the one forms definite platinum compounds, while the other depletes the oxygen concentration. When using ordinary air as the source of oxygen it is accordingly essential to employ low ammonia concentrations with air mixtures.

XIV—The following facts have been considered in reference to the comparative estimates of the various factors:

Cost of electrical energy at $0.004/k. w. h. per lb. HNO_3 (100 per cent)	$0.00071
Cost of platinum loss by dusting of sprouts at $115.00 per oz. HNO_3 (100 per cent)	$0.00031
Cost of 1 per cent drop in efficiency for NH_3 at $0.10 per lb. HNO_3 (100 per cent)	$0.0003

Average complete nitric acid charges for a whole oxidation plant:

Power, steam, etc., per lb. HNO_3 (100 per cent)	$0.0013
Operating labor, per lb. HNO_3 (100 per cent)	$0.0011
Repairs, labor, per lb. HNO_3 (100 per cent)	$0.00036

XV—That type of appliance which meets with the greatest success commercially is the one which is most nearly automatic and foolproof. If a given type of converter, with or without a multi-layer gauze, and without a suitable heat exchanger, is susceptible to poisons, variations in operation, etc., it is destined to be surpassed. The work at the U. S. Nitrate Plant No. 1 has been conducted in an effort to meet the commercial conditions. The enthusiasm and hard work of all the men associated with the project has greatly aided in the excellent results that were obtained.

XVI—The most essential factors involved in the choice of a commercial catalyst for use in the oxidation of ammonia are:

(1) High temperature of the intake gas phase.

(2) High catalyst temperature.

(3) High oxygen concentration.

(4) Controlled contact time with catalyst.

These are all interdependent. It is also desirable to have:

(5) Maximum oxidation with minimum weight of platinum.

(6) Utilization of the heat of reaction.

(7) Minimum catalyst free space with maximum catalyst surface per unit weight.

(8) Elimination of sudden expansion effects from abrupt excessive temperature changes from gas to catalyst.

THE INFLUENCE OF ESTER TRANSPOSITION IN THE DETERMINATION OF SAPONIFICATION NUMBERS

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Received June 20, 1919

INTRODUCTION

The following directions for obtaining the saponification value of an oil are taken from "The Volatile Oils" by Gildemeister and Hoffmann, second edition, translated by Kremers, Vol. 1, p. 572: "The saponification is conducted in a wide-necked flask of potash glass of 100 cc. capacity. A glass tube about 1 m. in length and passing through a stopper serves as a reflux condenser." As this book is published under the auspices of one of the large manufacturers of essential oils, it may be taken that this description represents the usual practice in the determination of saponification numbers and ester values. As the ester is frequently the valuable constituent in an essential oil, the saponification number or ester value is a matter of importance. It should be further noted that in actual practice a tube less than 1 m. long is frequently used as an air condenser.

Redfield[2] has made a study of the effect of the use of various forms of condensers in the assay of peppermint oil. He says, "One possible source of error that seems to have received no attention is the low efficiency of the reflux condenser that is employed. Any oil lost through incomplete condensation would, obviously, cause low results." He used three different condensers and six different peppermint oils and obtained striking results. Using a sample containing 8.01 per cent of ester, the poorest condenser gave 0.33 per cent low with a maximum variation from 0.20 per cent to 0.40 per cent. This 0.33 per cent is an error of 4.20 per cent on the total of 8.01 per cent. Using the acetylated oil, in which the ester amounted to 65.08 per cent, the poorest condenser gave results averaging 4.87 per cent low, varying from 3.54 per cent to 6.92 per cent in individual analyses. This last result with its variation of 6.92 per cent low shows an error of 10.6 per cent figured on the amount present. Redfield does not go into the reasons for this great loss further than the statement above quoted, but his results are important. Menthol commands a high price, and peppermint oil is valuable on account of its menthol content. Therefore an error of 10 per cent in the estimation of this constituent is serious. The poorest condenser that Redfield used is probably as good as those frequently employed. Redfield's work has an important bearing on the estimation of esters in general, which is a scientific problem as well as a practical one.

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[1] The experimental work except the preparation of some of the samples of esters was carried out at Tarkio College by A. M. Pardee.

[2] This Journal, 6 (1914), 401.

As Redfield says, "Any oil lost through incomplete condensation would, obviously, cause low results." In the oil with which Redfield worked the ester present was menthyl acetate, which boils at 222.4° according to Oppenheim,[1] or 227.8°, according to Kishner.[2] It does not seem probable that any appreciable amount of a substance of such a high boiling point, certainly not 5 per cent or 10 per cent of it, would be likely to escape through even a poor condenser. Some other explanation must be sought. It has been shown by Bertoni,[3] Saloman,[4] Kossel and Kruger,[5] Henriques,[6] Bacon,[7] Kreman,[8] Sudborough,[9] Bruni and Contardi,[10] Haller,[11] Berthelot,[12] Komnenos,[13] Pfannl,[14] Reid,[15] Madinaveitia,[16] Kolhatkar,[17] Qua and McLaren,[18] Wren and Still,[19] Wilcox and Brunel,[20] and others, that when an ester derived from one alcohol is dissolved in another alcohol, the second alcohol replaces the first in part, the reaction coming to equilibrium when certain concentrations are reached. Bertoni found this reaction to be extremely rapid with nitrites, but with ordinary esters, in the absence of catalysts, it is extremely slow, probably as slow as the esterification of an alcohol by an organic acid, but like esterification it is enormously accelerated by relatively small amounts of strong acids. Reid[21] has shown that sodium alcoholates are some 4,000 times more effective than an equivalent amount of hydrochloric acid. In a roughly quantitative experiment he found that methyl benzoate is transformed in ethyl alcohol solution by one per cent of its equivalent of sodium ethylate at the rate of 3 per cent per minute at 25°. Anderson and Pierce[22] find for the same temperature that methyl benzoate is 25 per cent saponified in 90 per cent ethyl alcohol in 108 min. by 111 per cent of its equivalent of sodium alcoholate. As the alcohol contained 10 per cent of water in this case the velocities are not strictly comparable, but it appears that the transformation of methyl benzoate into ethyl benzoate is some 1500 times as rapid as is its saponification. While the saponification is half complete in 4 hrs., the alcoholysis is probably nearly complete in several minutes. Anderson and Pierce find the saponification of acetates to be six or seven times as rapid as that of the benzoates and we may assume that, correspondingly, the alcoholysis of acetates is considerably more rapid than that of benzoates.

Henriques[1] many years ago concluded that in the saponification of glycerides, etc., by alcoholic potash the transformation of the glyceride into the ethyl ester is the first reaction, which is followed by the saponification of the ethyl ester. The results of Anderson and Pierce[2] beautifully confirm this conclusion. They find that methyl, ethyl, normal propyl, isobutyl, isoamyl, and benzyl acetates are saponified at exactly the same rate in methyl alcohol. As all of these esters must have been transformed into methyl acetate almost completely, within a few seconds, in the large excess of methyl alcohol used as solvent, they were actually measuring the rate of saponification of methyl acetate in each case and should have obtained the same velocity as they did. They obtained exactly similar results with these esters in ethyl and also in amyl alcohol; also with methyl and ethyl benzoates. With phenyl acetate, which is an ester of a different class, different results were obtained. On the other hand they find very different rates of saponification with methyl, ethyl, and propyl acetates, 0.1136, 0.0639, and 0.0435, respectively, in water solution.

Returning to the usual method of quantitative saponification of ethereal oils in which 0.2 g. of, say, menthyl acetate is added to 10 cc. alcoholic potash, there are 150 times as many molecules of ethyl alcohol present as of the menthyl acetate and we may expect its transformation into ethyl acetate to be practically complete within a few seconds. Now we have an entirely different problem; we have to provide such a condensing arrangement as will prevent the escape of ethyl acetate. As this ester boils at 77.4° and has a molecular weight of only 88, we can see that there would be danger of loss by its escape unless an efficient condenser is used.

A simple qualitative experiment, which is readily tried and which will convince anyone of ester transformation, is to add a few drops of odorless tri-acetin, b. p. 258°, to 10 cc. of 2 *N* alcoholic potash or soda in a dish. A strong odor of ethyl acetate is at once apparent.

It may seem remarkable that more difficulty has not been encountered with saponification work. In the case of linalyl acetate, terpinyl acetate, and acetates of other tertiary alcohols, this transformation does not seem to take place with anything like such rapidity. In many oils the acid is some other than acetic and the ethyl esters of such acids do not boil at such low temperatures as ethyl acetate and consequently are not so liable to escape through the condenser. Thus the methyl salicylate or oil of wintergreen would, by such transformation, give ethyl salicylate which is even less volatile than the original ester and would be in no danger of escaping.

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[1] *Ann.*, **120** (1861), 351.

[2] *J. Russ. Soc.*, **27**, 480.

[3] *Gazz. ital.*, **12** (1882), 435.

[4] *Ber.*, **8** (1875), 1509.

[5] *J. prakt. Chem.*, [2] **39** (1889), 157.

[6] *Z. angew. Chem.*, **1898**, 338.

[7] *Am. Chem. J.*, **33** (1905), 79.

[8] *Monatsh.*, **26** (1905), 783; **27** (1906), 410; **29** (1908), 23.

[9] *Proc. Chem. Sac.*, **21**, 87; *Centbl.*, **1** (1905), 1234.

[10] *Gazz. ital.*, **36** (1906), 356.

[11] *Campt. rend.*, **143** (1907), 657.

[12] *Ibid.*, **143** (1907), 717.

[13] *Monatsh.*, **31** (1910), 687; **32** (1911), 77.

[14] *Ibid.*, **31** (1910), 301.

[15] *Am. Chem. J.*, **46** (1911), 479.

[16] *Ann. soc. espoñ. fis. quim.*, **12** (1914), 426; *Chem. Abs.*, **9**, 2643.

[17] *J. Indian Inst. Sci.*, **1** (1915), 107; *Chem. Abs.*, **9**, 2762.

[18] THIS JOURNAL, **38** (1916), 1905.

[19] *Ibid.*, **38** (1916), 1821.

[20] *J. Chem. Soc.*, **111** (1917), 1019

[21] *Am. Chem. J.*, **46** (1911), 506.

[22] *J. Phys. Chem.*, **22** (1918), 44.

[1] *Z. angew. Chem.*, **1898**, 344.

[2] *J. Phys. Chem.*, **22** (1918), 55.

Rupp and Lehmann[1] recommend the use of glass-stoppered flasks in saponification instead of flasks with reflux condensers.

Winkler[2] has advised the use of propyl alcohol instead of ethyl alcohol in saponification work. He notes that it is a better solvent for fats than ethyl alcohol and has a higher boiling point so that no reflux condenser is required. He worked only with fats and waxes. Had he used acetic esters he might have obtained higher values on account of the less volatility of propyl esters as compared with ethyl.

To test this point two esters were chosen, benzyl acetate boiling at 206°, and methyl benzoate boiling at 198.6°. If the low results with poor condensation are due to a loss of the original ester, there should be nearly the same loss with these two esters, since their volatility is nearly the same; but if, by ester transposition, the one gives ethyl acetate, greatly increasing the volatility, while the other yields ethyl benzoate, decreasing the volatility somewhat, the acetate only should show loss with poor condensers. The experiments justified this expectation.

If instead of ethyl alcohol we use methyl alcohol as the medium, far greater losses are to be expected with the benzyl acetate, since methyl acetate boils at 54° and would, if formed, escape rapidly, while there would be no change in the volatility of the methyl benzoate. With alcohols of higher molecular weight, less volatile esters will be formed by alcoholysis and the losses should be still less. Accordingly comparative runs were made with isobutyl, normal butyl, and isoamyl alcohols. Experiments were made also with benzyl formate, b. p. 202°, since methyl formate, b. p. 32°, is still more volatile than the acetate.

APPARATUS AND MATERIALS

The apparatus for saponification was as simple as possible, duplicating the description quoted as standard. Resistance-glass flasks, round bottom, 100 cc. capacity, with 18 mm. ring neck, were connected by corks to pieces of thin-walled glass tubing, 12 mm. in diameter and a meter in length, which served as reflux condensers. Five such flasks used in each series were fitted into 87 mm. openings on the cover of a large water bath. All could be raised and lowered simultaneously, thus making the heating uniform.

The alcohols used, methyl, ethyl, isobutyl, normal butyl, and isoamyl, were of commercial purity. Each was treated with potassium hydroxide for 24 hrs. and distilled before use. The first two of these alcohols thus purified contained 5 per cent water, which was necessary for the saponification. Sufficient water was added to the other alcoholate solutions at the time of saponification to insure complete reaction between the alcoholic alkali solution and the ester.

The standard alcoholic alkali solutions were prepared by adding sufficient sodium metal to the various alcohols to make approximately $N/5$ strength. These solutions were allowed to stand 24 hrs. before standardizing against $N/10$ hydrochloric acid, which was in turn standardized by the silver chloride gravimetric method. The same 10 cc. pipette was used for measuring out the alcoholates for standardization and for the saponifications.

Of the esters used some of the samples were good commercial products and some were prepared by the usual methods. Only the formate calls for special attention.

One sample of benzyl formate, H, was made according to the method of Behal,[1] except that as anhydrous formic acid was not at hand, a 90 per cent acid was used with a corresponding excess of acetic anhydride. On account of the nearness of the boiling points of benzyl formate, 203°, and benzyl alcohol, 206°, fractionation is of little use for purification. The main fraction of the product, boiling between 199° and 202°, was used without further purification. From the analysis below it appears that it contained about 87 per cent ester.

The other sample, I, was made by ester transposition, and as this reaction has been but little studied with formates, this experiment is of some interest. In 40 g. benzyl alcohol, 0.15 g. sodium was dissolved and 50 g. methyl formate added. A considerable precipitate was formed. The mixture stood for three days at room temperature.

Water was added, the oil washed four times with water, dried, and distilled, 29 g. of it passing over between 197° and 200°, leaving 2 g. of residue. Analysis showed about 52 per cent ester in the product, proving that the reaction had taken place as expected.

PROCEDURE

Samples of the esters, 0.2 to 0.3 g., were weighed into the flasks, and 10 cc. of the alcoholate added to each. The flasks were put on the steam bath for exactly 1 hr., after which 50 cc. of carbon dioxide-free water were added to each and the excess of alkali titrated, using phenolphthalein as indicator. Care was taken throughout the work to make the results comparable.

RESULTS

The results are given in Tables I to V, inclusive, all of one run being in a single line, the average of the run being in the last column. The averages were taken before discarding the second decimals of the individual results. The results in a single run are more strictly comparable than those from different runs which were made at different times and with different standard alcoholate solutions.

DISCUSSION OF RESULTS

The results with isobutyl alcohol are high and unreliable. The end points in the titrations of its solutions were difficult to obtain and the isobutyl alcoholic alkali changed strength from day to day. The isoamyl solution did not titrate well and saponification was in some cases evidently incomplete. The results with these two alcohols may be left out of the discussion.

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[1] *Apoth.-Ztg.*, **24**, 972; *Chem. Abs.*, **4** (1910), 1910.

[2] *Z. angew. Chem.*, **24** (1911), 636.

[1] *Ann. chim. phys.*, [7] **20** (1900), 421.

Table I—Methyl Benzoate—Sample A, 98.51 Per cent; Sample B, 99.25 Per cent

No.	Sample	Per cent Ester Found					Average
		Methyl Alcohol Solution					
1	A	94.7	97.0	94.4	93.7	94.2	94.80
2	B	95.6	96.2	96.0	95.6	95.1	95.68
3	B	95.5	94.7	96.6	95.3	95.3	95.48
4	B	95.5	95.8	95.8	95.3	....	95.63
5	B	98.8	97.8	96.0	97.6	97.3	97.58
		Ethyl Alcohol Solution					
6	A	99.3	98.7	98.2	98.3	....	98.64
7	A	97.7	98.5	98.3	97.9	....	98.10
8	A	98.2	98.2	98.7	97.9	98.9	98.38
9	B	99.1	98.4	98.7	99.0	99.5	98.93
10	B	99.5	98.8	99.5	100.2	99.9	99.80
11	B	99.5	99.3	99.7	99.3	99.5	99.45
12	B	99.6	98.8	98.3	99.2	....	98.96
13	B	99.4	98.7	98.9	99.0	98.9	99.00
		Isobutyl Alcohol Solution					
14	B	100.6	102.0	100.2	.....	....	100.9
15	B	100.6	102.1	102.4	100.1	....	101.3
16	B	99.8	100.8	101.2	101.3	....	100.6
17	A	....	.....	.....	.....	....	.....
		Normal Butyl Alcobol Solution					
17	A	99.3	98.3	99.0	....	....	98.91
18	B	98.5	98.9	99.3	100.4	....	99.38
19	B	98.7	99.3	99.4	99.8	....	99.30
		Isoamyl Alcohol Solution					
20	B	96.1	95.4	95.4	98.8	93.3	95.79

Considering Table I, we find the average result in methyl alcohol solution to be 3.27 per cent low, the highest figure being only 0.41 per cent low. The vigorous boiling of the methyl alcohol may have driven out some of the methyl benzoate vapor, or the saponification may have been incomplete, since Anderson and Pierce found saponification in methyl alcohol seven times as slow as in ethyl alcohol.

In ethyl alcohol solution the average variation from the accepted values is 0.39 per cent, the average divergence of a single determination from the mean of its own series is 0.26 per cent. Comparing the average results on Sample B in ethyl alcohol, 99.25 per cent, with 99.34 per cent found in normal butyl alcohol, we find that there has been no appreciable loss of ester. Excellent results were obtained in both ethyl and normal butyl alcohols.

Table II—Benzyl Acetate—Samples C, D, and E, 99.58 Per cent

No.	Sample	Per cent Ester Found					Average
		Methyl Alcohol Solution					
21	C	25.4	26.4	22.1	24.9	26.9	25.1
22	C	19.3	21.2	20.2	21.2	22.4	20.9
23	C	14.6	27.0	15.7	18.1	18.7	18.8
24	C[1]	71.8	61.1	65.6	62.5	61.2	64.4
25	D	51.3	52.2	48.7	49.6	48.5	50.1
26	D	27.4	26.6	33.0	30.7	27.7	29.1
27	E	30.0	22.0	25.6	29.8	27.1	26.7
28	E	15.4	28.3	38.10	49.9	21.6	30.6
		Ethyl Alcohol Solution					
29	C	92.5	93.3	93.3	93.4	94.2	93.33
30	C	91.5	92.1	92.0	92.1	92.7	92.08
31	C	90.3	90.3	90.4	91.6	....	90.65
32	C	90.6	93.1	92.0	93.2	....	92.22
33	C	91.6	90.0	91.2	90.1	90.8	90.99
34	D	95.0	93.6	93.5	94.1	94.5	94.13
35	D	94.8	95.1	96.8	96.1	95.0	95.23
36	E	97.6	97.3	97.7	97.8	98.3	97.71
37	E	98.2	97.4	97.3	98.5	99.4	97.87
		Isobutyl Alcohol Solution					
38	E	101.6	101.2	101.2	102.3	101.2	101.48
39	E	98.8	101.5	100.6	100.7	....	100.6
		Normal Butyl Alcohol Solution					
40	E	99.3	99.1	99.1	99.4	99.5	99.30
41	E	99.5	100.4	99.2	100.0	100.3	99.86
		Isoamyl Alcohol Solution					
42	C	89.9	90.2	89.6	86.0	89.8	89.86
43	C	89.4	90.0	89.5	90.2	90.5	89.91
44	D	92.6	93.1	85.1	78.9	91.4	87.14
45	D	87.1	87.7	91.7	92.3	93.1	92.37

[1] Water-cooled coil condenser.

Table III—Ethyl Benzoate

No.	Per cent Ester Found					Average
	Methyl Alcohol Solution					
46	98.1	98.3	99.2	99.1	....	98.70
47	98.8	97.9	98.5	98.0	....	98.32
	Ethyl Alcobol Solution					
48	99.0	98.1	98.9	98.8	99.5	98.88
	Normal Butyl Alcohol Solution					
49	99.1	99.6	99.3	99.6	99.7	99.48
50	99.6	98.8	98.9	98.4	97.5	98.64
	Isobutyl Alcohol Solution					
51	98.9	99.5	99.7	99.6	100.8	99.69
52	97.8	98.7	97.9	98.8	....	98.31

Table IV—Benzoyl Benzoate

No.	Per cent Ester Found					Average
	Methyl Alcohol Solution					
53	98.7	98.4	99.1	98.6	98.6	97.72
	Ethyl Alcohol Solution					
54	97.9	98.2	98.2	98.7	98.0	98.19
	Normal Butyl Alcohol Solution					
55	98.1	97.8	98.5	97.8	98.5	98.14
56	98.8	98.3	97.4	98.5	98.9	98.40
	Isobutyl Alcohol Solution					
57	98.9	99.1	98.8	99.2	99.1	99.01

Turning to Table II we find just what was expected. The results in methyl alcohol solution except those of Runs 24 and 25 are extremely low, averaging only 25 per cent of the ester present. They are also very irregular, varying all the way from 15.4 per cent to 49.9 per cent in a haphazard fashion. No explanation can be given for the comparatively high results in Run 25. It is possible that saponification had largely taken place before the heating began. In Run 24, water-cooled coil condensers were used and even here the figures obtained are only two-thirds of what they should be.

With ethyl alcohol the results are more irregular than they should be. A close comparison can be made of Runs 36 and 37 with Sample E, which average 1.89 per cent lower than the average value found in normal butyl alcohol solution. There has been a slight loss of ethyl acetate.

The results in normal butyl alcohol are entirely satisfactory.

From Tables III and IV we find that satisfactory results are obtained in all of the alcohols, those in methyl alcohol being only a trifle low.

Table V—Benzyl Formate—Sample H, 86.92 Per cent; Sample I 52.63 Per cent

No.	Sample	Per cent Ester Found					Average
		Methyl Alcobol Solution					
52	H	68.1	68.3	68.1	66.2	64.4	67.02
53	I	49.8	50.4	48.5	49.5	48.3	49.51
		Ethyl Alcohol Solution					
54	H	85.1	84.8	84.5	84.7	84.5	84.70
55	I	48.5	51.7	51.4	51.4	51.5	51.52
		Normal Butyl Alcohol Solution					
56	H	87.2	86.7	86.8	87.0	87.1	86.92
57	I	52.4	53.0	52.8	52.6	52.4	52.63
		Isobutyl Alcohol Solution					
58	H	87.4	88.1	87.5	87.7	88.1	87.77
59	I	52.3	52.3	52.2	52.3	52.4	52.31

The results of Table V, at first sight, are surprising, those in methyl alcohol with Sample H being 20 per cent low and with Sample I only 2 per cent low. In ethyl alcohol they are 2 per cent and 1 per cent low.

The explanation is furnished by the work of Anderson and Pierce.[1] They find that methyl formate, in methyl alcohol solution, at 25°, is 54 per cent saponified in 1.68 min. Under the same conditions methyl acetate requires 245 min. for 50 per cent saponification. Or taking the average values of their velocity constants, the formate is saponified 350 times as rapidly as the acetate. It is probable that the methyl formate formed was nearly all saponified before the flasks could be put on the steam bath.

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[1] *J. Phys. Chem.*, **22** (1918), 55.

It appears that normal butyl alcohol, which can now be obtained in great purity at a moderate price, offers many advantages as a medium in which to carry on saponification. We have found this alcohol particularly suited for the quantitative saponification of fats, waxes, etc., results on which will be published shortly.

CONCLUSIONS

1—The alcoholysis of esters is to be taken into account in quantitative saponification.

2—Low results are to be expected when acetates are saponified in ethyl alcohol solution unless good condensers are used.

3—Normal butyl alcohol appears to be the best medium in which to carry on saponifications.

OIL-FIELD EMULSIONS

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PROPERTIES AND TREATMENT OF OIL-FIELD EMULSIONS FROM THE GOOSE CREEK (TEXAS) FIELD

The infiltration of water into the oil sands in drilling operations has been the source of much trouble and expense to the oil producer and refiner and there have been various methods advocated for shutting off water from wells.[2] Not only does the inflow of water decrease the productivity of the oil-bearing sands, but there is increased cost of production due to the expense of pumping water and replacing corroded tubing, casing pumps, and other fixtures.

From still another standpoint, also, the water has a detrimental effect in oil production. This arises from the fact that the water, mixing with the oil under the conditions of production, forms emulsions with the oil. The stability of the emulsions so formed varies considerably, not only for different fields and different wells in the same field but even for the same well during different periods of productivity. From certain emulsions the water separates upon standing; others are decidedly permanent in nature and show no tendency to separate, and it is these more stable ones which give the most trouble to the producer and refiner.

The amount of water varies from traces up to 60 per cent or more, but the majority of emulsions contain about 25 per cent. It has been assumed by many workers in the oil fields that all these will separate either oil or water, leaving an emulsion that is an exactly equal mixture of oil and water and to this they have given the name of "B. S." The term originated in the fact that when oil containing water, even a trace, is stored in large tanks, such as are in use at the pipe line pumping stations, there gradually accumulates a sediment known as "bottom settlings." These bottom settlings usually contain about 50 per cent water and considerable asphalt. It is very doubtful, however, whether all the emulsions will have this ratio as their settling end-point. By adding water to some of the more stable oil-field emulsions and agitating the mixture, it has been found possible to prepare emulsions containing as high as 90 per cent water which were quite stable and showed no appreciable separation after months of standing.

In order to be salable, or classed as "pipe line" oil and accepted by the transporting companies, a crude oil must contain no more than 2 per cent water. This is a purely arbitrary limit that has been fixed by the operating companies in accordance with their experience in refining. This necessitates, however, some treatment of the emulsions in the field.

PROCESSES FOR SEPARATION OF WATER

(1) FILTRATION PROCESS—The process of filtration has very little bearing on the treatment of oil-field emulsions, since it would not be possible to handle large quantities of oil economically, even if it were otherwise feasible. These filtering devices have been applied mainly to the separation of lubricating oils from water. The filtering medium is wetted initially with the external or dispersing phase and hence is not wetted during the filtration by the internal or dispersed phase. The tendency, however, is to cause a clogging of the filter. The filtering process has been improved somewhat by combining it with a certain electrical treatment.[1]

(2) EVAPORATION PROCESS—This method consists in heating the emulsion in open tanks or pits by means of coils containing superheated steam. It is uneconomical from the standpoint of fuel consumption and oil-evaporation loss, but oil production has been notorious for its wasteful methods and, until recent years, possibly even to this day, most of the dehydration of emulsions has been accomplished in this way. The fuel consumption is roughly 25 barrels of fuel oil per 1000 barrels of oil recovered. The oil-evaporation loss is about 5 per cent, depending upon the nature of the oil treated as regards the percentage of low boiling constituents. The heating of emulsions preparatory to other treatment is advantageous, but this heating is usually limited to a temperature of from 150° to 180° F. and is carried out in closed systems.

(3*a*) ELECTRICAL PROCESS. ALTERNATING CURRENT —The pioneer patent in the electrical treatment of oil-field emulsions was taken out by F. G. Cottrell.[2] This process depends for the demulsification upon the action of high potential alternating current electricity. The water is dispersed as finely divided globules throughout the oil and these are caused to coalesce by the action of the electrostatic forces. Quoting from the patent:

> These globules are thereby subject to electrostatic forces dependent upon the relative potentials and dielectric constants

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[1] Read at a meeting of the Southeast Texas Section of the American Chemical Society, at Houston, Texas, May 31, 1919.

[2] F. B. Tough, "Methods of Shutting Off Water in Oil and Gas Wells," Bureau of Mines *Bulletin* 163.

[1] Cottrell, U. S. Patent 987,114 (1911).

[2] Cottrell and Speed, U. S. Patent 987,115 (March 21, 1911).

of the materials in contact, and caused to coalesce into masses which may be readily removed from the body of the oil by well-known processes, such as settling.

The Petroleum Rectifying Company, of California, operating under this and other patents, has installed a number of plants in California, Oklahoma and Kansas.

(3*b*) ELECTRICAL PROCESS. DIRECT CURRENT—This process consists in passing the emulsion between electrodes connected to a source of direct current electricity with a potential of from 250 to 400 volts, with a current varying from a few milli-amperes to 10 amperes. The patent[1] under which the direct-current electrical treatment is operated claims that the process depends upon cataphoresis or electrical migration. The original experiments which served as a starting point for the development of this patented process were performed by the author with the help of Mr. G. W. Jones in May 1917, and the idea was based upon the known migration of colloidal particles when subjected to electrical stress.[2] We will see later, in the consideration of our experimental data, that this migration of particles must be a factor. Some electrolysis doubtless takes place since the electrodes are only about $^1/_8$ in. apart and at times a considerable current passes.

(4) CENTRIFUGAL PROCESS—The application of the centrifuge to the separation of water from these emulsions is rather limited. It is mainly useful in separating the last traces of water which have been discharged by other means. Thus it is used in the final step of the electrical treatment.

(5) CHEMICAL PROCESSES—The possibilities along the line of chemical treatment will be apparent from a consideration of our results and from the discussion of the action of certain treating compounds already on the market.

(6) GENERAL PROCESSES—Very often a number of the different methods are applied so that one supplements the others. The treatment of oil-field emulsions practiced by the Gulf Production Company in the Goose Creek (Texas) field consists of a combination of closed heating, settling, direct current electrical treatment and final separation of the remaining portions of the water by means of the centrifuge. Settling may be resorted to between the various stages of the treatment and the oil may be subjected to more than one electrical treatment, if necessary. In this combined process there is very little loss of the lighter fractions through evaporation and the fuel consumption is only about 10 barrels of fuel oil per 1000 barrels of oil recovered.

THEORETICAL CONSIDERATION OF THE MECHANISM OF COLLOIDAL SOLUTION AND EMULSIONS

The stability of colloidal solutions has been explained as due to the formation of surface films on the dispersed particles, preventing them from coalescing. These films may be either electrical or nonelectrical, or both, and when they are destroyed, agglomeration and precipitation of the particles occur. That electrical films may function in preventing coalescence, due to the repulsion of like charges, has been recognized for a long time. The fact that there was a movement of colloidal particles when subjected to electrical stress was recognized by Linder and Picton,[1] and this migration could only be indicative of the existence of charge of definite polarity on the particles themselves. In line with the general theory of the protecting action of surface films, it is assumed that these electrical films are formed by the preferential adsorption of an ion of an electrolyte. The fact that charged colloidal particles are discharged by solutions of electrolytes, due to the adsorption of an ion carrying a charge opposite to that already on the particles, is in accord with this surface condensation of ions. It was shown by Picton and Linder[2] that the precipitated material was contaminated by the electrolyte, and particularly by that ion of the electrolyte which, due to its charge being opposite to that of the colloidal particle, functioned as the effective precipitating agent. Hardy's[3] assumption that the ion of the electrolyte, having the same charge as that of the particles, had no effect in the precipitation is probably unreliable and it has also been shown that the point of coagulation does not always correspond to the point of electrical neutrality. It is clearly recognized, however, that ion adsorption plays a rôle.

It is usually assumed that emulsions are a special type of colloidal solution and that they differ from ordinary liquid-solid colloidal systems to a greater extent than could be explained, by the fact that the disperse phase is a liquid instead of a solid.

That ions may function as emulsifying agents, analogous to their action of forming protective films on colloidal particles, seems entirely possible and the work of certain investigators seems to indicate that they do so. Thus, the investigations of Wilson[4] and of von Lerch[5] on the curvature of the interfaces between nonmiscible liquids, point, according to Bancroft,[6] to ion adsorption. Ellis[7] has even prepared emulsions which owe their stability to ion adsorption. In working with phenol-water mixtures it was noticed that the "cloud" formed upon the separation of the second liquid layer from a saturated solution of phenol in water persisted for hours. It is not unlikely that any slight stability which this phenol water emulsion has is due to hydrogen ion adsorption. Work is in progress on the three-component system, phenol–water–acetic acid, and the preliminary results indicate that the clouds formed in this system are more permanent than in the two-component system, phenol–water.

With a liquid as the disperse phase, however, it is not surprising that in general it should require a rather tough coherent film such as could be obtained only from solid particles. The ordinary emulsifying agents are themselves colloids and the conditions for regulating which liquid shall function as the disperse phase have been very well defined. Thus, according to Bancroft,[1] "A hydrophile colloid will tend to make water the dispersing phase, while a hydrophobe colloid will tend to make water the disperse phase." Even in such cases, where the films protecting the disperse phase are colloids, we have charges upon the particles in so far as the colloids themselves carried charges.

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[1] Seibert and Brady, U. S. Patent 1,290,369 (January 7, 1919).

[2] *J. Chem. Soc.*, **67** (1895), 63.

[1] *J Chem. Soc.*, **67** (1895), 63.

[2] *Loc. cit.*

[3] *Z. phys Chem.*, **33** (1900), 385.

[4] *J. Chem. Soc*, **1** (1848), 174.

[5] Drude's *Ann.*, **9** (1902), 434.

J. Phys. Chem., **19** (1915), 276, 280.

[7] *Z. phys. Chem.*, **80** (1912), 597.

EXPERIMENTAL

The emulsions studied were obtained in the Goose Creek (Texas) field and, although they may or may not be representative of oil-field emulsions in general, the results are interesting, nevertheless, from the standpoint of the general theory of emulsification. As they are representative of the more stable of the Goose Creek emulsions, the results are applicable to the general treatment of the product of this region.

These emulsions are systems of water dispersed in oil as an external phase. This is clearly shown by the ordinary tests applied in the identification of phases in such systems.[2] One of the most satisfactory tests in such cases is the treatment of the emulsion with some component of one of the two phases. If the emulsion spreads in or mixes with the added component or phase, that phase is evidently the external or dispersing phase. It was found that these emulsions mixed readily with dry crude oil in all proportions but did not mix with water or salt solutions. The emulsified water contains salt (sodium chloride, etc.), sometimes up to 10 per cent, and if such aqueous solution was the external phase the emulsions would conduct the current readily. As a matter of fact, with electrodes 2 in. apart and with a potential difference of 250 volts impressed, it is not possible to notice any deflection of the needle of a sensitive milliammeter placed in the circuit. Clearly, then, the oil is the external phase.

The particles of water forming the disperse or internal phase are very finely divided and are apparent as a "fuzziness" in thin layers of the oil. Practical oil-field men identify the presence of water in an oil by placing a few drops on a piece of glass and holding vertically so as to allow drainage and form a thin film of oil on the surface of the glass. A dry oil will appear as a clear, amber colored film, while an oil containing water will appear "fuzzy."

THE CHARGE ON THE PARTICLES—The attempt was made to get some information as to whether or not the particles were charged and, if so, the nature of that charge. A drop of the emulsion was placed on the slide of a microscope and two small platinum wires, connected into a 70-volt direct current circuit, were brought into contact with the drop of oil. It was impossible to get any results in this way, due to the capillary effects, since the oil flowed from the center and collected about both wires. Some of the emulsion was then placed in a cell, Fig. 1, and a potential of 70 volts was impressed after connecting the electrodes to a direct-current circuit. It was thought that it might be possible to get an indication of migration and hence of the charges on the particles by measuring the percentage of water in the two sides of the cell after the experiment had run for some time. The cell was left connected for 22 hrs. and at the end of that time considerable change in outward appearances had taken place in the two sides. The color of the original emulsion was a yellow-brown. After the 22-hr. run the oil in the positive side of the cell was much darker than the original emulsion and the oil in the negative side much lighter. The presence of more water particles would cause a lighter appearance, and the less the number of particles the nearer would the color approach the dark green-black of dry oil. This would seem to indicate that water particles had migrated from the positive to the negative side, and that there was a positive charge on the particles. In neither side was there any discharged free water in the bottom of the cell. When determinations of the water content on the two sides of the cell were made, no difference was found, all the oil in each side of the cell being tested. This result was rather surprising in view of the quite evident color changes that had taken place. After running a number of these tests, however, it was noticed that upon withdrawing the electrodes from the oil a mass of water particles adhered to the positive electrode, and upon examination it was found that the water particles in the negative side had been driven to the outside against the side of the vessel. This clearly pointed to a negative charge on the particles. In that case they would be attracted to the positive electrode and collect around it, causing a darkening in the outside layer of the oil as they migrated to the center. On the negative side they would be repelled by the electrode and forced to the outside layers near the glass, causing a lighter color. It was therefore decided that the particles were negatively charged.

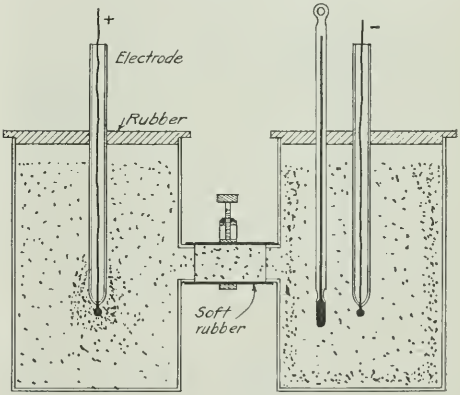

FIG. 1—MIGRATION OF PARTICLES

PRECIPITATION BY ELECTROLYTES—If the particles were negatively charged, this charge might be neutralized by some readily adsorbed cation, and precipitation brought about. Hydrogen ion is more strongly adsorbed than most ions, as a rule, and it was therefore decided to try the effect of various concentrations of different acids. The experiments were carried out as follows: 200 cc. of the emulsion containing 25 per cent water were placed in a 500 cc. ground-glass-stoppered graduate and 50 cc. of the acid added. The mixture was then shaken on an electrically driven shaking machine for 20 min. in order to insure intimate contact. It was then allowed to stand for 22 hrs., after which the percentage water in the oil layer was determined.

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[1] *J. Phys. Chem.*, **19** (1915), 275. NOTE—The term hydrophobe colloid is applied to a substance forming a colloidal solution in some nonaqueous solvent and not doing so in water; the term hydrophile colloid to a substance forming a colloidal solution in water but not in the nonaqueous liquids considered.

[2] *J. Phys. Chem.*, **18** (1914), 34

When more water was added and the mixture agitated, it was possible to incorporate this added water with the emulsion, the color becoming lighter with increasing proportions of water. In the case of the addition of hydrochloric acid solution, a change was quickly apparent as the emulsion became darker colored almost immediately. The notes in connection with Table I, where the results with hydrochloric acid are tabulated, refer to this color change.

TABLE I

Number	Emulsion. Cc.	Acid Mixture		Water in Oil Layer. Per cent	Hydrogen Ion Concentration Normality	Color when Taken from Shaker	Remarks
		Conc. HCl Cc.	Water Cc.				
1...	200	2.0	48.0	36.0	4.89×10^{-1}	Yellow	Total emulsification
2...	200	5.0	45.0	15.0	6.02	Dark brown	Honeycomb structure
3...	200	7.5	42.5	7.0	8.87	Brown-black	Separation of good
4...	200	10.0	40.0	1.0	10.00	Green-black	Oil started at once

Temperature 25° C.

In order to show that the hydrogen ion was functioning as the precipitating agent, a series of experiments was performed, using sulfuric and acetic acids. The results of these experiments are given in Tables II and III.

TABLE II

Number	Emulsion Cc.	Acid Mixture		Water in Oil Layer Per cent	Hydrogen Ion Concentration Normality	Color when Taken from Shaker
		Conc. H_2SO_4 Cc.	Water Cc.			
1.. .	200	5	45	19.0	1.88×10^{-1}	Dark brown
2.. .	200	10	40	12.0	3.04	Dark brown
3 . .	200	20	30	2.5	3.86	Black-green
4 ..	200	30	20	1.75	10.00	Black-green

Temperature 25° C.

TABLE III

Number	Emulsion Cc.	Acid Mixture		Water in Oil Layer Per cent	Hydrogen Ion Concentration Normality	Color when Taken from Shaker
		Glacial Acetic Cc.	Water Cc.			
1.....	200	2	48	40.0	... ..	Yellow-brown
2	200	5	45	38.0	0.45×10^{-1}	Dark yellow-brown
3 . ..	200	10	40	30.0	0.86	Brown-black
4 ...	200	20	30	30.0	2.51	Dark brown-black
5 .	200	35	15	5.0	8 53	Green-black

Temperature 25° C

The hydrogen ion concentrations, expressed in Tables I to III, were determined by means of the hydrogen electrode. In our experiments we had added 50 cc. of an acid mixture to 200 cc. of the emulsion and, as the emulsion was 25 per cent water, we always had 100 cc. of acid solution in the system. For the hydrogen ion concentration measurements the quantities of acid used in the various experiments to make up the 50 cc. of added mixture were diluted to 100 cc. The e. m. f. of the cell (normal calomel electrode–hydrogen electrode in the given acid solution) was balanced against a known e. m. f. and the hydrogen ion concentration computed according to the following equation:[1]

$$E = 0.058 \log 1/c + 0.28$$

When the H ion concentrations are plotted against the water percentage in the separated oil layer the curves as given in Fig. 2 are obtained.

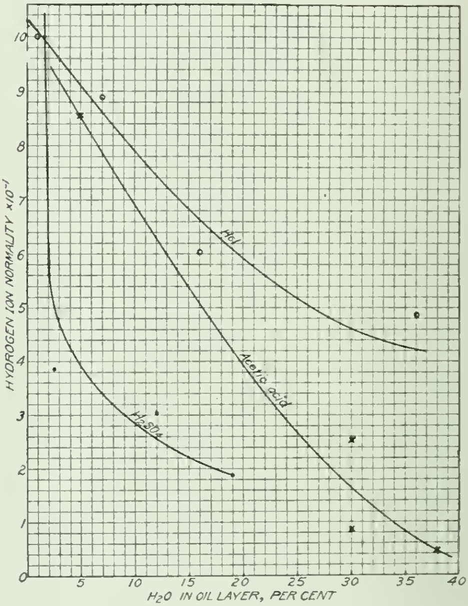

FIG. 2—PRECIPITATION OF WATER PARTICLES BY HYDROGEN ION

Since it is not safe to follow Hardy[2] and assume that the ion carrying a charge opposite to that of the colloidal particles is the only effective ion, we would expect the hydrogen ion concentration necessary for complete discharge to vary somewhat; and particularly, on account of the preferential adsorption of ions, we would not expect the curves to coincide. Since, however, the hydrogen ion concentration necessary for the complete discharge of the water from the oil ranges around the value 10.0×10^{-1} normal, we can safely ascribe the precipitation to the effect of hydrogen ion, and our previous conclusions regarding the existence of a negative charge on the particles are substantiated.

Since the hydrogen ion neutralized the charge on the particles and precipitated the emulsion, it ought to be possible to discharge them in a similar manner by means of other strongly adsorbed cations. In line with the generally strong adsorption of ferric ion by various substances, and from the general consideration of the stronger precipitating power of polyvalent ions over that of ions of less valency, it was of interest to see what effect ferric ion would have. 200 cc. of the emulsion were treated with ferric chloride solution, as in the previous experiments with acids. Table IV gives the results of these tests.

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[1] Hildebrand, *J. Am Chem Soc.*, **35** (1913), 847.

[2] *Z phys. Chem.*, **33** (1900), 385.

TABLE IV

Number	Added Mixture: $FeCl_3$[1] Solution Cc.	Added Mixture: Water Cc.	Sp Gr. of Added Mixture	Water in Oil Layer Per cent
1	2.0	48.0	......	22.0
2	5.0	45.0	......	8.0
3	7.5	42.5	......	2.0
4	10.0	40.0	1.0610	1.5
5	20.0	30.0	1.1213	1.5
6	35.0	15.0	1.2050	0.5
7	50.0	0.0	1.2878	0.5

Temperature 25° C.

[1] Ferric chloride solution used in making up added mixture contained 66.24 g. of $FeCl_3$ per 100 cc.

REMARKS

Sample 4, after 22 hrs., contained 150 cc. of a black jelly with a layer of good oil above it. This jelly flowed easily and upon being disturbed broke up, depositing most of its water phase.

Sample 5, after 22 hrs., contained 125 cc. of black jelly very similar in action to that of Sample 4.

Samples 6 and 7, after 22 hrs., contained 180 cc. of stiff black jelly which was very stable. Good oil on top.

As in the case of hydrogen ion, we found that ferric ion discharged the emulsions. In lower concentrations the action was perfectly regular, but in the higher concentrations as in Expts. 4 to 7, we did not get a separation of the water phase itself, but obtained jellies of varying stability. The jellies obtained in Expts. 6 and 7 were very stable indeed; the cylinders containing them could be turned over and the supernatant oil drained off without disturbing or displacing them. Upon removing some of these jellies with a spatula they were found to be of the consistency of a very stiff apple butter, and transference or manipulation did not destroy them. Jelly 6 contained 60 per cent by volume of ferric chloride solution, and Jelly 7 contained 56 per cent. Jellies 4 and 5 were very unstable.

Although hydrogen ion resulting from the hydrolysis of the ferric chloride might have had some effect, particularly in Expts. 1 to 5, nevertheless the results of Expts. 6 and 7 clearly show the influence of the ferric ion. It might seem, since the jellies contained from 56 to 60 per cent of the water phase, that they resulted from a partial precipitation or insufficient positive ion adsorption. If this were the case, hydrogen ion should cause the discharge of these jellies into their separate phases. Samples of the two stiff jellies were treated with varying concentrations of hydrogen ion but in no case were the jellies destroyed. Evidently the particles of which the jellies were composed were no longer negatively charged or they would have been discharged by the hydrogen ion of the acid.

It is a well-known fact that certain colloids are positively or negatively charged, depending upon the character of the dispersing phase. Thus albumin is positively charged in acid solution[1] and negatively charged in alkaline solution.[2] Since the jellies we obtained were evidently not negatively charged it seems possible that the adsorption of ferric ions had carried the particles past the neutral or isoelectric point and that they were now positively charged. Since a stiff jelly of this character does not lend itself to measurement of migration in an electric field, the only other way seemed to lie in testing the effect of strongly adsorbed anions upon the jelly.

Just as hydrogen ion is one of the most strongly adsorbed cations, so hydroxyl ion is one of the most strongly adsorbed anions. It was not possible, however, to use hydroxyl ion to identify the charge on the jelly because of the ferric ion present. In a study of the order of adsorption of anions by precipitated barium sulfate the following order was found:[3]

Ferrocyanide > nitrate > nitrite > chlorate > permanganate > ferricyanide > chloride > bromide > cyanide > sulfocyanate > iodide.

Since nitrate ion is strongly adsorbed and there is no interfering action between it and the ions already present, it was selected as being suitable for our purpose. Sodium ion is known to be very little adsorbed, hence we used sodium nitrate in these experiments. When the gel obtained from the original treatment of the emulsion with ferric chloride was treated with a saturated solution (25° C.) of sodium nitrate, it was destroyed and the oil freed. It seemed, then, that the jelly was composed of positively charged particles.

In line with the action of these gels, ferric nitrate should precipitate the original emulsion without the formation of jellies, since the adsorption of nitrate ion would counteract to some extent at least the adsorption of ferric ion. Experiments were carried out to determine the effect of the simultaneous adsorption of ferric and nitrate ions on the emulsion. Table V shows the results of these determinations.

TABLE V

Number	Emulsion Cc.	Added Mixture: $Fe(NO_3)_3$ Solution Cc.	Added Mixture: Water Cc.	Separated: Solution Cc.	Separated: Sponge Cc.	Water in Oil Layer Per cent	Color after Standing 22 hrs.
1	200	5	45	5	None	32.0	Light brown
2	200	10	40	15	70	16.0	Brown
3	200	15	35	25	80	5.0	Dark brown
4	200	25	25	65	35	1.0	Dark brown
5	200	50	0	65	35	0.5	Green-black

The temperature of liquids during these experiments was 25° C. The sponge obtained in these experiments was very mobile and broke up upon the slightest agitation. Ferric nitrate solution used in making up the added mixtures contained 67.32 g. $Fe(NO_{33})$ per 100 cc.

These results with ferric nitrate clearly show that both ions have an effect in the precipitation and bear out our previous conclusions as to the strong adsorption of nitrate ion.

In order to see to what extent the increase in the density of the water phase influenced these precipitation results, a number of experiments were run, using saturated solutions (25° C.) of sodium sulfate, sodium chloride, sodium carbonate and sodium bicarbonate, but in no case did we obtain a discharge of the water particles.

EFFECT OF ORGANIC SOLVENTS—There are a number of methods in use for determining the percentage of water in an emulsion. Most books on petroleum analysis recommend the distillation method. This consists in adding toluene to a sample of the emulsion and distilling. The added toluene keeps down the troublesome frothing that usually occurs when undiluted emulsions are distilled. The water, toluene, and certain light portions of the oil come over, and as they separate into layers without emulsifying the percentage of water can be computed. The method most in vogue in the oil fields, on account of its simplicity, is to add a high-grade gasoline to a sample and centrifuge it. The volume percentage of water can then be read off directly on the graduated centrifuge glass. Usually the results obtained by these two methods will check, but occasionally the emulsions will not respond to this gasoline treatment. It has been found that ether is even better than gasoline for this centrifuge method. The explanation usually offered for this method is that the addition augments the difference in density of the two phases, causing a greater tendency to settle. This may be true to some extent but it cannot be the only effect, as will be shown.

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[1] Hofmeister's *Beitr. chem. Physiol.*, **5** (1904), 27.

[2] Pflüger's *Archiv.*, **24** (1887), 247; cf. Bancroft, *J. Phys. Chem.*, **19** (1915), 350.

[3] Weiser and Sherrick, *J. Phys. Chem.*, **23** (1919), 205.

The existence of negative charges on the water particles has been shown, but it is doubtful whether the ions alone function as the emulsifying agent. It seems probable that the ions which are responsible for the charge are condensed on solid particles which in turn form the protecting films. In many of these emulsions there is considerable earthy material and it may be possible that this material serves as the emulsifying agent, being itself peptized by ion adsorption.

On the other hand, the asphalt in these oils may be responsible for the formation of the films. Some slight amount of asphalt is present in colloidal solution in these crude petroleums, as a hydrophobe colloid, and would cause the formation of an emulsion with water as the disperse phase. It was found to be possible to prepare an emulsion of salt solution in pure white paraffin oil by using 0.5 per cent of asphalt. The emulsion so formed was not as stable as the natural oil-field emulsions and no definite charge on the particles could be identified; nevertheless it was much more stable than the suspension made by shaking the pure oil with the salt solution.

It is entirely possible that this system is even more complicated than the previous assumptions would indicate. Thus we might have the earthy material adsorbing asphalt or other heavy hydrocarbons from the crude oil, and these in turn forming protective films about the water particles, with the consequent adsorption of ions to impart a charge to the particles.

Richardson[1] found that the earthy matter in Trinidad asphalt had a high adsorption capacity for the bitumen of the asphalt.

Now in so far as the asphalt, either alone or condensed upon earthy matter, acted as the emulsifying agent, it would seem that the action of the ether in facilitating a separation of the two liquid phases might be due to the solvent action of the ether on the asphalt rather than to any augmentation of the difference in density of the two phases. If this were so, a liquid, miscible with the oil phase and having a high solvent action on the asphalt, should discharge the emulsion even if it had the same density as the emulsion itself. In order to test this point the specific gravity of the emulsion was determined and a mixture of ether and carbon disulfide having this same specific gravity was made. When this solvent mixture was added to a sample of the emulsion it discharged the water even more readily than ether alone. It would seem then that the action of these organic solvents was due to solvent effects rather than to differences in density.

COMMERCIAL COMPOUNDS AND CHEMICALS FOR TREATING OIL-FIELD EMULSIONS

There are on the market certain compounds for the treatment of oil-field emulsions. These compounds are usually crude soaps or sodium salts of sulfonic acids, obtained by sulfonating either a coal-tar oil or a petroleum.[1] All of such compounds examined were hydrophile colloids, which seems to be the explanation for their action in discharging these oil-field emulsions.

Just as there is selective adsorption of ions, so there is selective adsorption of colloids, and certain hydrophile colloids might have a much greater tendency than others to destroy an emulsion formed by means of a given hydrophobe colloid. Just as precipitation of colloidal particles is due to the adsorption of an ion with a charge opposite to that upon the particles, so colloids of opposite charges precipitate one another. But in the destruction of an emulsion formed by a hydrophobe colloid it is not necessary that the hydrophile colloid be of an opposite charge. Thus we have negatively charged soap particles precipitating the negatively charged water particles of these emulsions.

These properties and actions of oil-field emulsions would indicate in a general way the methods for their efficient treatment. It must be borne in mind, however, that the emulsions from different fields may differ markedly in properties and therefore might require entirely different treatment. In so far as they do differ, each field would have to be investigated in order to indicate the best method of treatment. In any case, it may be advantageous to combine a number of processes to supplement one another.

The author hopes to be able to procure samples so that representative emulsions from the other oil fields of the country may be examined.

SUMMARY

The results of this investigation are summarized as follows:

1—The emulsions occurring in the Goose Creek (Texas) oil fields have been studied.

2—These emulsions consist of salt solution as disperse phase and oil containing asphalt as the dispersing phase.

3—The water particles migrate to the anode under electrical stress and are therefore negatively charged.

4—Strongly adsorbed cations neutralize the negative charge on the particles and precipitate the water.

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[1] *J Phys. Chem.*, **19** (1915), 245–6.

[1] Francis and Rogers, U. S. Patent 1,299,385 (1919).

5—Ferric ion is adsorbed to such an extent that it will carry the particles over from a negative charge through the isoelectric point to a condition of positive charge in a manner analogous to the reversal of charge on albumin particles.

6—From the experiments with ferric chloride and ferric nitrate it is apparent that both ions of an added electrolyte are effective in precipitation of the charged particles.

7—The decrease in stability of these emulsions upon the addition of ether is probably due to the solvent action of the ether on the asphalt rather than to any increase in the difference in density of the two liquid phases. An ether-carbon disulfide mixture of the same gravity as the emulsion will discharge the water.

8—The action of certain commercial treating compounds is probably due to the fact that they are hydrophile colloids. A hydrophile colloid should discharge an emulsion formed by the use of a hydrophobe colloid, while a hydrophobe colloid should discharge an emulsion formed by the use of a hydrophile colloid.

ACKNOWLEDGMENT

In conclusion, the author wishes to thank Mr. E. T. Gregg for aid and helpful suggestions, and Dr. F. M. Seibert and Mr. J. Van der Henst for procuring samples.

TESTING THE MILDEW RESISTANCE OF TEXTILES[1]

By B. S. Levine and F. P. Veitch

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A study of the fundamental factors determining the effectiveness and durability of processes of waterproofing and mildewproofing textile fabrics, such as cotton duck and cotton canvas, was undertaken with the primary object of finding simple formulas and methods for treating cloth which are applicable for small-scale use on the farm and also suitable for use by commercial treating plants. Prerequisites for successful work on the main problem are, of course, suitable methods for determining water and mildew resistance. The method here described, which is not regarded as final but subject to improvement with experience and greater knowledge of the problems involved, has been used for the past two years and has proved to be useful in judging the probable serviceability of mildew-resistant treatments. The methods used for testing the water resistance of fabrics are described in a separate paper.[2]

Mildewing is due to the development of various mold growths on and in the fabrics. The number of species responsible for the deterioration is large, but chief among them are species of *Alternaria*, of *Cladosporium*, and some *Mucors*. The simultaneous occurrence of different kinds of molds seems to play an important part, and the production of pink and yellowish discolorations is probably due, at least in some cases, to the growth of both a *Mucor* and a mold producing a substance having a pink appearance in alkaline or neutral reaction and a yellow one in an acid reaction.

Gueguen[1] is of the opinion that the spores causing the mildewing of fabrics are usually introduced into the fibers by the dead parts of the parent cotton plant, where they have been either in a dormant or germinating state, and concludes that mildew is hardly ever due to contamination of the fabric after weaving.

The presence in the air of spores of cellulose-destroying fungi has been demonstrated by McBeth and Scales,[2] who have isolated from plates exposed to air contamination over a dozen cellulose-destroying organisms, among which *Cladosporium herbarum* has been identified. Davis, Dreyfus and Holland[3] have shown that astonishingly large numbers of mold spores rain into the mill vats containing sizing materials used on the component threads, thereby becoming introduced into the woven fabric.

We have repeatedly mildewed pieces of treated and untreated fabrics by inoculating their surfaces with pure cultures of *Cladosporium*, *Alternaria*, and other molds, and have found that, under laboratory conditions, converted canvas may be completely destroyed by several species of *Aspergillus*.

Sterilized duck inoculated with spores and mycelial fragments of species of *Alternaria* and of *Cladosporium* and incubated for two weeks, developed mold growth which, at the end of another two weeks, entered deeply into the fabric. Furthermore, heavy fabrics, subjected to certain finishing processes having a sterilizing effect on the preëxisting mold spores and mycelial fragments, readily mildew under favorable field conditions. It is clear, therefore, that even canvas apparently free from original mold impregnation will mildew if exposed to air contamination and to conditions encouraging mold growth.

METHODS USED TO DETERMINE MILDEW RESISTANCE

Tests for mildew resistance of fabrics have been in use heretofore. One, occasionally followed, is, briefly, to bury a sample of the cloth under ground at a depth of 12 to 15 in. for a period extending over one month. The ground is kept moist by occasional watering. The condition of the fabric at the end of the test period is considered to indicate the degree of mildew resistance.

This method may give valuable information regarding the resistance of fabrics to bacterial action, but its value for determining mildew resistance is questionable. Waksman[4] found that soil samples taken from a depth of 12 to 30 in. on plating out developed only *Zygorhynchus*, and that *Aspergillus*, *Alternaria*, *Cladosporium*, *Penicullium*, and other organisms commonly present in the soil had not appeared in the plates in 24 hrs.; while in the upper soil strata there may be 1,000,000 fungi per gram of soil. This, really, is a small number of organisms, as compared with the many millions of bacteria usually present. Canvas buried under ground would, therefore, be subject to bacterial rather than to fungus attack. That this is so, is indicated by the fact that cotton duck coated with a thin layer of paraffin remained practically unattacked when buried under ground for nearly a month, whereas mildew developed in less than a month when inoculated in the laboratory.

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[1] Read at the 57th Meeting of the American Chemical Society, Buffalo, N. Y., April 7 to 11, 1919.

[2] This Journal, **12** (1920), 26.

[1] *Compt. rend.*, **159** (1914), 781.

[2] U. S. Dept. of Agr., Bureau of Plant Industry, *Bulletin* **266**, pp. 24–25.

[3] "Sizing and Mildew in Cotton Cloth," **1880**, Palmer and Howe, Manchester.

[4] *Science*, N. S., **44** (1916), 320–23.

Furthermore, since it is generally recognized that different soils have different microbial flora, that species present under one combination of conditions may be absent under others even in the same soil, it is not practicable to standardize this method of testing.

Another method is to roll together several samples of the cloth to be tested with layers of fresh horse manure and of sawdust and keep for about a month in a moist condition. At the end of the period the condition of the cloth is observed, and if no deterioration is evident, the samples are again rolled up and left for another month or two.

Haubner,[1] Henneberg and Stohmann,[2] Knieriem,[3] Choukevitch[4] and others have shown that cellulose is fermented by bacteria in the intestinal tract of practically all animals, man included. It is reasonable to think, therefore, that cellulose-destroying bacteria abound in fresh feces, but that molds are practically absent. This statement has been confirmed in this laboratory. Finally, this procedure obviously cannot be standardized, and, because of its offensive character, is not suited for laboratory work.

The simplest and most useful method heretofore used is that of suspending the test sample in a closed jar containing some water. The jar is kept in a dark, preferably warm, room for 5 to 7 days. At the end of this period, the test is discontinued. This test, though subject to some criticism, is better than those previously described, since it can be easily conducted under standard conditions. The period of incubation usually employed, however, is entirely too short. We have found that certain fabrics, which have remained unattacked by molds for over a week, have proved to be susceptible to mildew and were completely overgrown in three weeks to one month of incubation. Davis, Dreyfus and Holland[5] have employed a procedure for testing the mildew resistance of cotton goods similar to the one just described, with a period of incubation from 40 to 50 days. In experiments on mildewing "pure cloth" the following results, among others, are given:

> "Seventh day.—Damp but nothing visible. Twelfth day.—Visible only under the microscope. Twentieth day.—Slight fructification. Twenty-eighth day.—Badly mildewed, brown spots, etc."

Their results, together with our observations, have convinced us that 30 days is the shortest allowable period of incubation when testing fabrics for mildew resistance.

A serviceable test for mildew resistance of textiles should include the following factors:

1—Aërobic conditions of growth.
2—Proper humidity.
3—Proper temperature.
4—Subdued light.
5—Sufficient period of incubation.
6—Standard conditions with regard to the controllable factors involved in the test.
7—Simplicity of procedure.

To meet these conditions the following procedure has been adopted. Cut six discs about $3^{1}/_{2}$ in. in diameter from the sample to be tested and place in running water at room temperature for at least 2 days. In the absence of running water place the discs in a beaker of water and change the water several times during the day. This soaking and washing is for the purpose of removing from the fabric as much of the water-soluble, germicidal and fungicidal substances as possible and also the fermentable material. If these are left in the fabric, they may suspend or hasten the development of the mildew spores, making it appear that the fabric is highly mildew-resistant or highly susceptible, whereas in practice the substances may be almost completely washed out by the first rain, and the resistance of the fabric become markedly different.

At the end of the period of soaking, place the discs between clean blotting papers or towels and remove excess of water by pressure. Place the discs in six bacteriological Petri plates containing 10 to 15 cc. of plain agar jelly free from nutrient matter, being careful that the plates do not become air-tight. The plates with the discs are incubated in a closed chamber at a temperature of 20° to 25° C. for 7 to 10 days. If they show a heavy and well-developed growth, the test is discontinued. If, however, the growth of mold is entirely absent or is merely starting, the discs are inoculated with stock cultures of *Alternaria*, *Cladosporium*, and a pink *Mucor*, and further incubated for from 3 to 4 weeks. The first period of incubation is designated for convenience as the "pre-inoculation period."

During the second period of incubation weekly examinations of the plates are made macroscopically and with the aid of the binocular microscope whenever necessary. The factors observed and taken into consideration, are:

1—Extent of contamination or so-called spontaneous growth.
2—Extent of inoculation growth.
3—Discoloration.
4—Strength of the fabric.
5—Nature of the predominating growth.

A rating on the basis of ten has been worked out which is, of course, arbitrary, and subject to future modification. Where results cannot be measured and expressed mathematically, precision cannot be expected. The definitions and ratings are based upon observable factors which do not lend themselves to definite measurement. They are, therefore, subject to errors introduced by the so-called individual equation. However, after some experience, the worker obtains a concrete understanding of the terms "very heavy," "heavy," "considerable," "fair," and "negligible."

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[1] *Amst-und Anzeigeblatt für die Landwirtschaftlichen Vereine der Königliche*, Sachson, **1854**.

[2] *Beitrage zur Begrundung einer rationellen Futterung der Wiederkouer*, Braunschweig, **1860-4**, 2 pts.

[3] *Z. biol.*, **21** (N. S. **3**) (1885), 67–139.

[4] *Ann. Inst. Pasteur*, **25** (1911), 247–276.

[5] *Loc. cit.*, p. 205.

The rating is based on one month's incubation.

Observations				
Contamination Growth	Inoculation Growth	Other Characteristics	Rating	Nomenclature
Very heavy[1]	....	Tendering of cloth	0	Mildew - susceptible
Very heavy[1]	....	Tendering not readily observable	1	Not mildew-resistant
Heavy[1]	....	Marked discoloration	2	
Heavy[1]	....	Visible discoloration	3	
Considerable	Fair	Slight discoloration	4	Negligibly mildew-resistant
Considerable	Negligible	No visible discoloration	5	Slightly mildew-resistant
Fair	Negligible	No visible discoloration	6	Considerably mildew-resistant
Negligible	Negligible	No visible discoloration	7	Mildew-resistant
Negligible	Visible only through binocular microscope	No discoloration	8	Highly mildew-resistant
Negligible	None	No discoloration	9	Very highly mildew-resistant
No	None	No discoloration	10	Mildew-proof

[1] Where the contamination growth is heavy the condition of the inoculation growth may be overlooked. In fact it is frequently overgrown by the spread of contamination molds.

Data permitting the comparison of the results of laboratory tests of the mildew resistance of textile fabrics by the above method with field exposures have been obtained, and, though at present still meager, are indicative of the value of the test. Pieces of treated and untreated cloth were stretched over frames in the form of tents and exposed to weather conditions in the vicinity of Washington for nearly a year. The samples were then brought into the laboratory and examined for mildew. The table shows the results of the laboratory test and outdoor exposure of some of the samples.

	Laboratory Test				
Number	Contamination Growth	Inoculation Growth	Other Characteristics	Rating	Exposure Test
34791[1]	Very heavy	....	No readily observable tendering of cloth	1	Heavily mildewed
34792[1]	Heavy	....	Marked discoloration	2	Black mildew
34780[1]	Heavy	....	Marked discoloration	2	Black and yellow mildew
34772	Heavy	....	Marked discoloration	2	Black and green mildew
34797	Heavy	....	Marked discoloration	2	Considerably mildewed
34856	Heavy	....	Marked discoloration	2	Black mildew
33309	Considerable	Fair	Slight discoloration	4	Some black mildew
34828	Considerable	Fair	Slight discoloration	4	Heavily mildewed
34832	Considerable	Fair	Slight discoloration	4	Mildewed
34834	Considerable	Fair	Slight discoloration	4	Mildewed
32409	Considerable	Negligible	No visible discoloration	5	Some black mildew
34826	Considerable	Negligible	No visible discoloration	5	Slightly mildewed
34748	Considerable	Negligible	No visible discoloration	5	Mildewed
33331	Fair	Negligible	No visible discoloration	6	No mildew
33460	Fair	Negligible	No visible discoloration	6	No mildew
32388	Negligible	Negligible	No visible discoloration	7	No mildew
33434	Negligible	Negligible	No visible discoloration	7	No mildew
32383	Negligible	Visible only through binocular microscope	No visible discoloration	8	No mildew
33017	Negligible	....	No visible discoloration	9	No mildew
33001	None	None	No visible discoloration	10	No mildew
33003	None	None	No visible discoloration	10	No mildew

[1] The first three samples were of untreated gray duck—the remainder were from treated material.

It will be seen from these preliminary results that samples which by the laboratory method give a resistance of six or better withstood exposure for a whole year under normal weather conditions near Washington, D. C. How much longer these fabrics will withstand exposure without mildewing is now being determined. The procedure can apparently be relied upon, especially in distinguishing between resistant and nonresistant treatments.

SUMMARY

I—The methods heretofore usually employed for testing mildew resistance of fabrics are outlined and their disadvantages pointed out.

II—A laboratory method is described which is simple in execution and the details of which have been standardized.

III—A rating on the scale of 10 and a system of nomenclature have been developed on the basis of laboratory observations. The practical significance of these underexposure conditions will be further studied and reported.

IV—A comparison has been made of the results of the laboratory test with results of exposure tests.

THE INFLUENCE OF THE METHOD OF MANUFACTURE ON THE USE OF CASEIN IN GLUE MAKING

By Samuel Butterman

Forest Products Laboratory, Madison, Wisconsin

Received August 20, 1919

The urgent necessity for a water-resistant glue for use in aircraft construction was realized immediately upon our entry into the war, but at that time, in this country, relatively little was known regarding its preparation. The severe weather conditions to which airplanes are subjected and the impracticability of covering all glued joints in a machine with a waterproof coating, led the Air Service of the War Department and the Bureau of Construction and Repair of the Navy Department to adopt very exacting requirements as to water resistance for all glue used in the manufacture of certain aircraft parts. The U. S. Forest Products Laboratory, Madison, Wis., was called upon to investigate this subject in order to obtain definite information as to the properties of, and methods of obtaining water-resistant glue.

Two types of water-resistant[1] glue have been successfully developed, one based on soluble blood albumin and the other on casein. Casein is practically insoluble in water, but in the presence of alkaline substances it forms solutions which are highly viscous and possessed of marked mucilaginous properties. If lime is present, these solutions soon "set," and on drying form a hard mass which does not redissolve in water. Such a mixture of casein, lime and other alkaline substance, to which certain other ingredients may be added to confer additional desirable properties, forms the so-called "waterproof" casein glues which are commercially available at the present time.

In the early work at this laboratory in the development of casein glue formulas it was found that shipments of casein from different sources, or often two shipments from the same maker, exhibited such marked differences in behavior that the glue formula had to be seriously altered for each sample of casein. This made it necessary to extend our study to cover the influence of the method of manufacturing casein on its use in glue.

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[1] F. L. Browne, "Water-resistant Glues," *Chem. & Met. Eng.*, **21** (1919), 136.

MANUFACTURE OF CASEIN

Casein occurs as the principal protein of milk, closely associated with lime and calcium phosphate in a form generally designated as calcium caseinate. The casein is obtained as a precipitate by freeing it more or less completely from this combination. The methods of doing this may be divided into two classes:

1—Acidification of milk. The acids commonly used are lactic, hydrochloric, and sulfuric.

2—Coagulation of milk by rennet.

For the sake of economy, casein is not made from whole milk. The milk is first passed through a cream separator to obtain butter-fat and the skimmed milk is used for the manufacture of casein. Although it is also possible to obtain casein from buttermilk, very little is made from it at the present time, and we shall therefore confine our discussion to skim-milk casein.

LACTIC ACID OR NATURAL-SOUR METHOD—In this method the necessary acidification is produced by the fermentation of the lactose of milk. The milk is allowed to stand at room temperature until the amount of lactic acid produced is almost enough to cause separation of the curd from the whey, and then warmed to about 130° F., whereupon the curd separates. The whey is drained off and the curd is sometimes washed with cold water. The curd is wrapped in cloth and pressed to remove the remaining whey or wash-water as far as possible, and dried by spreading it on trays in a drying tunnel through which air, at a temperature not over 130° F., circulates. This method of procedure is sometimes spoken of as the "vat" or "cottage cheese" method.

In order to avoid loss of time fresh skim milk is sometimes warmed and allowed to flow out of a pipe. From a neighboring vat a stream of warm, sour whey is allowed to flow in such a way that it mixes with the stream of skim milk, and the liquid falls into a third vat from which the whey is finally drained and the curd washed, pressed, and dried as before.

An excellent grade of natural-sour casein is made by the "ejector" method developed by the Bureau of Animal Industry.[1] The skim milk (or buttermilk) is allowed to sour until its acidity, as determined by titration with a standard alkali solution, using phenolphthalein as indicator, is 0.8 to 0.9 per cent, expressed as lactic acid. It is then allowed to run out of the tank through an ejector where it is rapidly heated by introducing steam, and to fall into a second tank where the curd collects on top. The whey is drained off and the curd washed, pressed, and dried.

METHOD OF COAGULATION WITH ACIDS—In this method the necessary acidification is produced by adding acid directly to the milk. This saves the time required for the production of lactic acid by natural souring.

The fresh skim milk is placed in a vat and heated with steam to about 120° F. About one pint of sulfuric acid (sp. gr. 1.84) for every 1,000 lbs. of milk is diluted with a gallon of water and added to the milk, which is gently stirred until the curd separates. The whey is drained off and the curd washed. It may then be pressed and dried, as in the case of natural-sour casein, or it may be "cooked." This process consists in covering the curd with water and heating to 170° to 175° F., when the curd collects in a semi-fluid, plastic, tough mass. The water is drained off, and the soft curd barreled and shipped.

By far the greater part of the commercial casein made in the United States is produced by the sulfuric acid method. In some creameries where the whey is later used for recovering lactose, hydrochloric acid is substituted, to avoid certain mechanical difficulties at a later point in the process.

J. L. Sammis, of the Dairy Department of the University of Wisconsin, has shown that by proper manipulation sulfuric acid curd can be made with as low ash content as natural-sour casein.[1]

THE GRAIN-CURD METHOD—The Bureau of Animal Industry has developed a method for making commercial casein by the hydrochloric acid method which gives a product of exceptional purity. This method has been successfully put into practice by at least one large creamery.

The method takes its name from the character of the curd when obtained from milk in which the hydrogen ion concentration is approximately that of the isoelectric point of casein, $P_H = 4.6$. This is easily controlled in practice by adding the dilute acid to the milk and testing small samples by means of methyl red, comparing the color with that of a stock solution of known hydrogen ion concentration. By the careful regulation of temperature and acidity the curd is easily freed from impurities.

METHOD OF COAGULATION WITH RENNET—Rennet casein is obtained by treating milk with rennet. Since no acid is formed during the process, the ash content of the caesin thus produced is very high.

CHARACTER OF COMMERCIAL CASEIN

Commercially available caseins are of the most diverse character. They range in quality from practically white, sweet smelling products relatively low in impurities, through light yellow to dark brown material with sour and highly offensive odors. The marked variation in behavior of caseins in various applications is shown by the specific preferences of different consumers for one type or another. Thus one manufacturer maintains that natural-sour casein alone is satisfactory for his purpose, whereas another stipulates that only mineral acid casein is to be furnished. In many instances scientific supervision is lacking; no explanation for this preference is given beyond some reason expressed in the vernacular of the trade and hence devoid of any significance to one not familiar with the particular application under consideration.

In our work in developing casein glue formulas, this wide dissimilarity in the caseins was a source of much difficulty because a formula which gave satisfactory results with one casein might fail completely with another. With any casein of reasonably good quality, however, it was possible by an alteration in the proportions of the ingredients of the formula to obtain a satisfactory glue. Investigations were therefore made into the causes of variation in commercial casein made by different methods and their effect upon the use of casein in glue.

The results of the first part of this work have already been published.[2] Over 300 samples of commercial casein, made by different methods and different makers, were analyzed for moisture, fat, ash, "acidity," and nitrogen, the last giving a measure of the organic impurities other than fat present. In

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[1] A. O. Dahlberg, "The Manufacture of Casein from Buttermilk or Skim Milk," U. S. Dept. of Agr., *Bulletin* **661**

[1] Work about to be published.

[2] F. L. Browne, "The Proximate Analysis of Casein," THIS JOURNAL, **11** (1919), 1019.

Table I are given the results of the analyses of samples of casein made at a large creamery by different methods. These results are typical of the casein produced at the present time by each of these methods:

TABLE I—RESULTS OF ANALYSES OF CASEIN MADE BY DIFFERENT METHODS

METHOD	Av. No. of Samples	Moisture Per cent	Fat (Moisture-free Basis) Per cent	Ash (Moisture-free Basis) Per cent			Nitrogen (Moisture Fat-Ash-free Basis) Per cent	Acidity[1] Cc.
				Max.	Min.	Av.		
Buttermilk	9	6.97	9.56	2.18	0.88	1.36	14.77	9.2
Grain curd	11	9.48	0.33	3.76	1.08	1.65	14.84	9.9
Natural sour	18	7.87	0.27	2.62	1.33	2.16	14.84	8.7
Sulfuric acid	34	7.81	0.35	5.36	3.02	4.05	14.46	7.6
Sulfuric cooked	8	8.89	0.12	5.58	3.92	4.25	15.04	5.9
Hydrochloric cooked	8	9.44	0.18	5.09	4.14	4.71	15.03	5.2
Hydrochloric acid	6	7.10	0.16	6.03	5.51	5.74	14.32	6.7
Rennet	3	8.29	0.63	8.39	7.18	7.97	14.41	7.9

[1] Acidity is expressed as cc. of *N*/10 sodium hydroxide solution required to dissolve 1 g. of moisture-, fat- and ash-free casein and give a solution neutral to phenolphthalein.

For skim-milk casein the moisture and fat contents are independent of the method of precipitating the curd, although the nitrogen content varies considerably. None of these seems to have much influence on the behavior of casein in glue. Further discussion will therefore be limited to the effect of ash content and "acidity."

INFLUENCE OF IMPURITIES ON USE OF CASEIN IN GLUE

It was early observed that caseins prepared by the three commercial methods—lactic acid, mineral acid, and rennet—show marked differences with respect to the quantity of water required to reduce the glue prepared from them to the same viscosity. In general, caseins of the same type require a quantity of water which varies within a definite range and is somewhat sharply differentiated from the quantity required by other types. Indeed, in most cases,[1] it is possible to name the method of manufacture by a mere observation of the relative amount of water required by the casein under investigation. From Table II it will be seen that this property closely parallels the ash content of the casein.

Since this variation in water requirement is by far the most serious one encountered in using any casein for glue making, a thorough study was made of the relation between water requirement and ash content of commercial caseins. For this purpose casein glue Formula 4 of this laboratory[2] was selected, and glues were made from a large number of commercial caseins of different kinds, the amount of water used in each case being varied until the desired viscosity was obtained. A similar study was made later with three entirely different glue formulas. The results obtained were similar in all cases; therefore the data given below seem to have general application to casein glues.

The method of procedure was as follows: 100 to 200 g. of dry, powdered casein were weighed and mixed with *x* parts of water. After soaking a few minutes until the casein was thoroughly wet, a suspension of lime containing one part of hydrated lime to 6 parts of water was stirred in. The amount of lime used in this suspension was equivalent to 15 per cent of the weight of casein used. Finally an amount of sodium silicate solution (sp. gr. 1.4) equal to 0.7 of the weight of casein was added, and the mixture was then vigorously stirred until all particles of casein had dissolved, giving a homogeneous mass. (In the following tables the "water-casein" ratio means the ratio of the total weight of water used to that of casein.) Among the characteristics observed in these glues were the consistency and glue "life." If the glue exhibited, by simple observation, a viscosity intermediate between a thin, watery mixture and a thick, heavy mixture, its consistency was recorded as "medium." Similarly a very high viscosity was described as "stiff." By the term "life" is meant the period of time between the preparation of the glue and the point where it becomes too thick to spread properly.

Seventy-two different caseins were tested in this way. A few typical samples selected at random are given in Table II.

TABLE II—INFLUENCE OF ASH AND ACIDITY ON VISCOSITY AND LIFE OF GLUE

TYPE OF CASEIN	Ash Per cent	Acidity Cc.	Ratio of Water to Casein	Consistency	Life Hrs.
Grain curd	1.28	...	2.3	Medium —	12.0
Lactic acid	1.43	7.4	2.4	Medium —	11.0
Lactic acid	1.43	7.6	2.4	Medium —	11.0
Lactic acid	1.44	9.0	2.4	Medium —	18.0
Lactic acid	1.49	7.9	2.5	Medium —	16.0
Lactic acid	1.62	8.8	2.4	Medium	8.5
Lactic acid	1.7	7.9	2.3	Medium	16.0
Lactic acid	1.81	8.6	2.5	Medium —	23.0
Lactic acid	1.81	8.5	2.4	Medium	12.0
Lactic acid	2.51	8.2	2.5	Medium	10.0
Lactic acid	2.62	10.6	2.5	Medium +	6.5
Sulfuric acid	2.64	7.0	2.5	Medium —	14.0
Grain curd	2.7	...	2.5	Medium	9.0
Sulfuric acid	3.02	9.1	3.0	Thin	18.0
Sulfuric acid	4.29	6.0	2.7	Medium	6.5
Sulfuric acid	4.91	7.1	2.7	Stiff —	5.5
Sulfuric acid	4.96	8.1	2.7	Medium +	5.0
Sulfuric acid	4.96	6.0	2.7	Stiff	6.5
Sulfuric acid	4.93	8.5	2.9	Medium +	9.0
Sulfuric acid	5.06	...	2.9	Medium	6.0
Sulfuric acid	5.08	8.2	2.9	Medium +	6.5
Sulfuric acid	5.10	8.4	3.1	Stiff +	3.0
Sulfuric acid	5.36	5.8	2.8	Stiff	6.0
Sulfuric acid	5.58	5.7	2.8	Medium +	7.0
Sulfuric acid	6.03	6.5	3.1	Stiff —	4.5
Rennet	8.59	5.5	3.7	Medium +	5.0

An examination of Table II will show the close relation between the ash content of casein and the water-casein ratio required to give a glue of medium consistency. This at once explains the variation in the behavior of casein made by different methods. It is to be noted that when a mineral acid casein is so made that its ash content lies in the same region as lactic acid casein, its water requirement approaches that of the latter. It should also be observed that there is no abrupt transition in the ash contents, and therefore in the water-casein ratios, of caseins made by different methods, but that they merge gradually into each other. The recent work of the Bureau of Animal Industry and of J. L. Sammis has shown that, under the proper conditions of manufacture, the ash content of mineral acid casein is as low as that of lactic acid casein, in which case there is no difference in the behavior of the products of the two methods.

It is interesting to note, as shown in Table III, the effect on the behavior of the casein after washing. Washing lowers the ash content and consequently the water-casein ratio required to produce a given

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[1] Caseins made by the method of Sammis or by the grain curd method are exceptions to this rule.

[2] U. S. Patent 1,291,396, granted to S. Butterman, and assigned to the United States.

TABLE III—EFFECT OF WASHING THE CURD ON THE BEHAVIOR OF THE CASEIN

TYPE OF CASEIN	Times Curd Washed	Ash Per cent	Acidity Cc.	Ratio of Water to Casein	Consistency	Life Hrs.
Lactic acid	0	2.51	8.2	2.5	Medium	10.0
Lactic acid	3	1.44	9.0	2.4	Medium —	18.0
Lactic acid	0	2.46	8.5	2.3	Medium +	7.5
Lactic acid	3	1.93	7.4	2.4	Medium —	11.0
Lactic acid	0	2.20	8.9	2.5	Medium	11.0
Lactic acid	3	1.49	7.9	2.5	Medium —	16.0
Lactic acid	0	2.62	10.6	2.5	Medium +	6.5
Lactic acid	3	1.33	9.0	2.4	Medium —	13.0
Sulfuric acid	1	5.58	5.7	2.8	Medium +	7.0
Sulfuric acid	2	3.55	6.2	2.8	Medium —	12.0
Sulfuric acid	0	4.40	6.5	2.8	Medium	6.5
Sulfuric acid	2	4.15	6.3	2.8	Medium —	9.0
Sulfuric acid	0	3.94	8.2	2.6	Medium	9.0
Sulfuric acid	Several	2.64	7.0	2.5	Medium —	14.0

viscosity. This is shown in the table either by the lower water-casein ratio or by the lower viscosity or longer life exhibited by the glues made from the lower ash caseins.

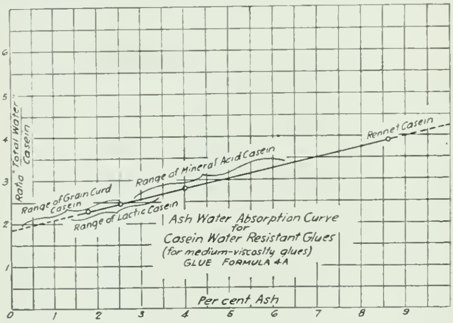

FIG. 1

CASEIN GLUE—CHARACTERISTIC CURVE

The general relations just discussed are presented in a very striking manner if a casein glue characteristic curve is constructed by plotting ash content against water-casein ratio. In Fig. 1 four typical points are plotted—one for each type discussed. The properties of each point have been selected to represent the average characteristics observed for these types. The data used for this curve are given in Table IV. The water-casein ratio in each case is such as to produce a glue of medium viscosity.

TABLE IV

TYPE OF CASEIN	Ash Per cent	Water Casein
Grain curd	1.8	2.3
Lactic acid	2.5	2.4
Mineral acid	4.0	2.8
Rennet	8.6	3.9

In Fig. 2 the values of ash and water-casein ratio necessary to give a glue of medium viscosity are plotted for 72 different samples of casein. The curve drawn coincides with Fig. 1. The average deviation from the straight line approaches 0.2 part of water. This is practically negligible because the water was not measured more closely than 0.1 part and the observation of viscosity is only approximate, so that the experimental error is at least 0.3 part; yet but two of the 72 points plotted exceed this experimental error.

In checking the data of Table II against this curve, it must be remembered that the curve is drawn for medium viscosity glues, and therefore it is necessary to correct roughly the water-casein ratio to conform to this viscosity wherever it was not actually observed. Table V illustrates such a correction in the case of two glues.

TABLE V

Ash Per cent	Water Casein Observed	Consistency	Water Casein Corrected	Consistency
6.03	3.1	Stiff —	3.3	Medium
1.43	2.40	Medium —	2.2	Medium

By extrapolation it can be predicted that an ash-free casein would require 1.85 parts of water. A sample of casein, made by the Van Slyke[1] method, was available whose ash content was 0.38 per cent. According to the graph such a casein should require 1.95 parts of water to make a glue of given viscosity. Investigation showed that 2.15 parts were actually required, which is well within the experimental error.

The curve in Fig. 1 represents an equation of the type

$$y = mx + c.$$

Hence if A is the ash content of the casein, and W the water-casein ratio required to give a glue of medium viscosity,

$$W = 0.24A + 1.85$$[2].

By making a determination of the ash content of a given sample of casein, it is therefore possible to tell at once the proper proportion of the ingredients required to mix it into a satisfactory glue, regardless of the method by which the casein has been prepared. It is therefore possible to use casein made by any of the commercial methods for making casein water-resistant glue and still obtain uniform results.

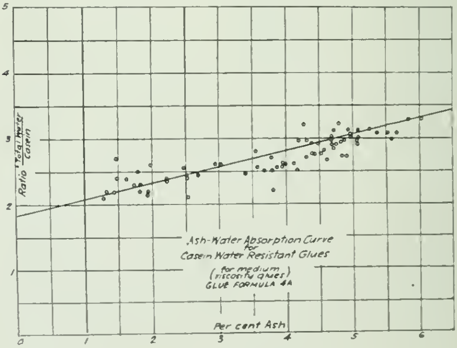

FIG. 2

SUMMARY

1—A brief description of the commercial methods of manufacturing casein is given.

2—The variation in the behavior of casein made by different methods when used in water-resistant glue is due to the variation in ash content.

3—Since the amount of water required to give a glue of medium viscosity is a linear function of the ash content, it is possible to plot a "glue characteristic curve" for any casein glue formula by means of which a uniform production of glue from casein made by any of the commercial methods can be insured.

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[1] *J. Biol. Chem.*, [1] **35** (1918).

[2] These constants apply to Formula 4 only

ALKALI FUSIONS. I—THE FUSION OF SODIUM *p*-CYMENE SULFONATE WITH SODIUM HYDROXIDE FOR THE PRODUCTION OF CARVACROL[1]

By H. D. Gibbs and Max Phillips

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INTRODUCTION

The study of a number of commercially important alkali fusions is under way in this laboratory. The investigation of the reaction between sodium *p*-cymene sulfonate and sodium hydroxide, involved in the production of carvacrol, is published at this time, not for the reason of its commercial importance, but because other work on cymene has been in progress in this laboratory for some time[2] and also because the work of Hixson and McKee[3] on the commercial manufacture of carvacrol which has appeared so recently describes a commercial procedure that appears to be open to improvement.

The usual method of conducting fusions in a fire-heated open kettle, with stirrer, is open to serious objections in many manufacturing operations, and is especially undesirable in laboratory studies for many reasons, among which may be mentioned local overheating, the change in the composition of the melt due to evaporation, the action of air which in some cases causes undesirable oxidation, and the fact that this method of studying reaction rates and conditions is very slow, because a number of hours are usually required for the determination of each point on the various curves involved.

We have devised an apparatus permitting of the determination of six points on a curve in a period of time only a little greater than that usually required for one point, and at the same time avoiding the other disadvantages above enumerated.

The results show that the fusions made in an autoclave give greatly increased yields, and a saving in chemicals and ease of operation over the open-kettle method.[4] The results differ materially from those of Hixson and McKee.

MATERIALS

SODIUM *p*-CYMENE SULFONATE—Cymene was obtained by purifying the crude "spruce turpentine" from a sulfite pulp mill by digesting with lime for several days, and distilling at a pressure of 5 mm. The distillate and about $^1/_5$ of its volume of 95 per cent sulfuric acid were placed in a vessel provided with a mechanical stirrer and agitated together for several hours at room temperature. After separating off the acid and washing the oil with water, fresh acid was added and the stirring continued until a portion of the oil after being washed with water, gave, at most, a very light yellow color when shaken with sulfuric acid. A total of 15 hrs. stirring with acid usually sufficed to give the desired product. The oil, washed free from sulfuric acid and dried over calcium chloride, was fractionated over sodium using a Glinsky still head. Practically all distilled over from 176.5° to 177.5°, leaving only a small amount of viscid material in the flask. 1000 cc. of the cymene fraction and 1600 cc. sulfuric acid (sp. gr. 1.84) were heated together on a water bath with constant mechanical stirring. This was continued until a test portion was completely soluble in water. The sulfonated product was treated with barium carbonate and the barium sulfonate obtained in the usual way. The solution of this salt was then carefully treated with a sodium carbonate solution, the barium carbonate filtered off, and the filtrate evaporated to dryness on the steam bath. The colorless residue was finely powdered and dried in a vacuum oven at 120°. This material was used in all of our fusion experiments. A sulfur analysis made on this product gave the following results:

Calc. for $C_{10}H_{13}.SO_3Na$: S, 13.55. Found: 13.51, 13.42

SODIUM HYDROXIDE—This was the "C. P." article purified with alcohol and assaying 98 per cent NaOH.

APPARATUS

The apparatus[1] used in our fusion experiments is shown in Fig. 1. It consists of a sheet iron tank, B, filled with solder to the level C, and insulated by means of asbestos walls H. The bath is heated with gas burners, D, and the temperature regulated by proper adjustment of the gas supply by means of valves F. The temperature is indicated by a thermometer inserted in well X. With careful attention the temperature of the bath may be maintained practically constant. The six tubes N, in which the fusion mixture is placed, are provided with screw caps and copper gaskets and may be screwed down so that they are gas-tight. The tubes are held in the carrier M by means of clamp O and screws P. The carrier may be raised or lowered by means of racks U and gears T operated through crank S. It is held in position when either raised or lowered by means of a ratchet gear V and stop W. The carrier is so constructed that it revolves in bearing Q moving on guides R, and driven by the motor J through the spur gear K, shafts Z and bevel gears L, the tumbling motion thus imparted to the tubes N insuring the complete and constant mixing of the contents. The whole is mounted on angle iron frame A supplied with suitable castors to make the apparatus portable.

EXPERIMENTAL METHODS

ALKALI FUSIONS—In ascertaining the conditions for obtaining the highest yield of carvacrol it was neces-

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[1] Presented at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

[2] THIS JOURNAL, **10** (1918), 453; **11** (1919), 455, 1130.

[3] *Ibid.*, **10** (1918), 982; McKee, U. S. Patent 1,265,800 (1918).

[4] Although Hixson and McKee employed a cylindrical steel vessel which could be tightly closed, fitted with a stirrer and thermometer, and heated in a eutectic mixture of sodium and potassium nitrates with accurate temperature control, they record no experiments in which the vessel was closed to prevent escape of gases.

A covered fusion vessel was employed in order that a condenser could be attached to recover considerable quantities of cymene formed during the reaction. Taking this recovered cymene into consideration their best yield was 64.65 per cent [52.31 (carvacrol) + 12.34 (cymene calc. as carvacrol) = 64.65], except in one large-scale operation when it figured 66.4 per cent [57.2 (carvacrol) + 9.2 (cymene calc. as carvacrol) = 66.4].

They state: "Without a cover the fusion mass thickens, due to reaction with oxygen of the air, and the volatile oil which distils off is lost."

[1] The apparatus was constructed by R. Hellbach and G. Orange, of the mechanical staff of this laboratory.

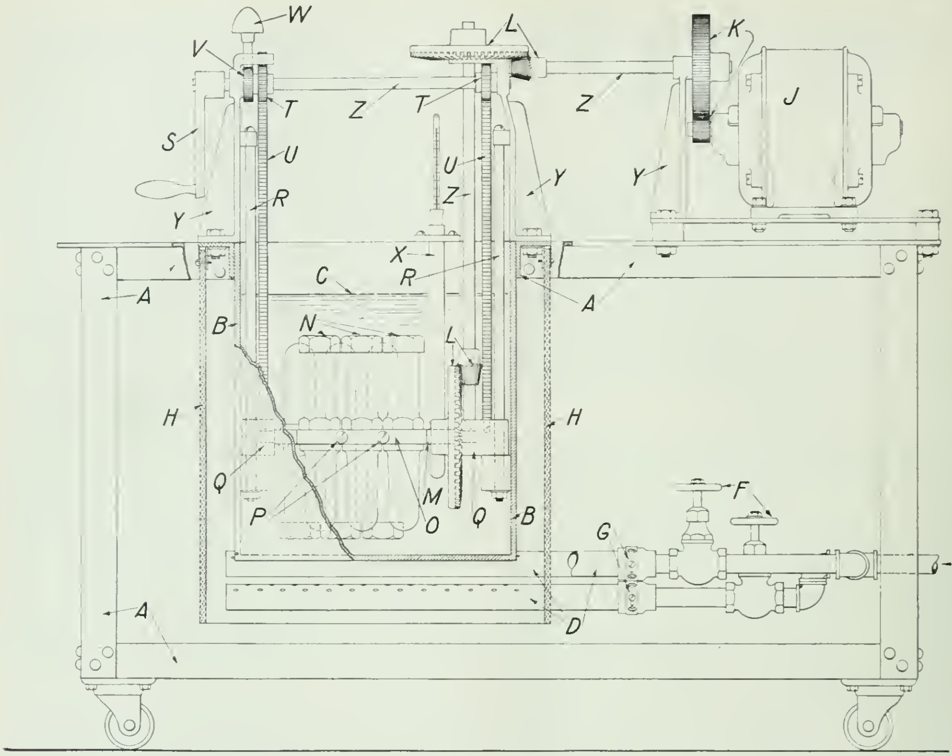

Fig. 1—Apparatus for Alkali Fusion

sary to determine experimentally the four following factors:

1—Proper fusion temperature.
2—Proper fusion period.
3—Ratio of sodium hydroxide to the sodium cymene sulfonate.
4—Relation between the carvacrol yield and the percentage of water in the charge.

Accordingly, 0.1 mole of the sulfonate mixed with the theoretical amount of alkali (0.2 mole) was placed in each one of the six tubes and the latter rotated in the metal bath kept at a constant temperature. At certain intervals of time, namely, 1, 2, 4, 6, 8, and 10 hrs., a tube was removed, suddenly chilled with cold water and analyzed for its carvacrol content. Experiments were conducted at 280°, 325°, 350°, and 360°, and from the data thus obtained, the proper fusion period and temperature were deduced. Having determined this, an experiment was then carried out using the same amount of sulfonate but different amounts of sodium hydroxide for each tube, the fusion being conducted at the optimum temperature and fusion period determined by the previous experiments. In the same manner, the effect of the addition of water to the fusion mixture was determined by adding a known amount of water to each tube, using the optimum conditions of the other factors previously determined experimentally.

ISOLATION OF THE CARVACROL—The fused mass was removed from the tubes by means of hot water, filtered, acidulated with dilute sulfuric acid, and extracted with ether. On evaporating the solvent, a residue consisting of crude carvacrol was obtained.

METHOD OF ANALYSIS—The amount of total carvacrol obtained from the evaporation of the ether was determined and a weighed sample analyzed for its carvacrol content by means of the Messinger and Vortman[1] method, as subsequently modified by Kremers and Schreiner.[2] Instead, however, of using an iodine solution of known normality, standardization was made against pure carvacrol, employing conditions identical in all analyses. This we consider the only satisfactory method for determining the yields of carvacrol. A criticism of the methods employed by other workers is to be found under the heading "Discussion."

EXPERIMENTAL DATA

EFFECT OF THE TIME AND TEMPERATURE OF THE FUSION ON THE CARVACROL YIELD—Using the same amount of sulfonate in each case ($^1/_{10}$ mole) and the theoretical amount of sodium hydroxide (0.2 mole) four fusion experiments were carried out at different temperatures, namely, 280°, 325°, 350°, and 360°. The results obtained are recorded in Table I, and graphically in Fig. 2, Curves 1, 4 and 5.

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[1] *Ber.*, **23** (1890), 2753.

[2] *Pharm. Rev.*, **14** (1896), 221; Allen's "Commercial Organic Analysis," 4th Ed., **4**, 399.

Table I—Time and Temperature of Fusion

Constants—Ratio of sodium p-cymene sulfonate to sodium hydroxide

Variables—Temperature and time

Number	Fusion Period Hrs.	Carvacrol Yield Expressed as Per cent of Theoretical 280°	325°	350°
1	1	1.2	25.0	37.5
2	2	2.8	39.8	60.6
3	4	5.2	56.1	71.6
4	6	9.2	59.3	74.1
5	8	11.7	62.3	72.8
6	10	15.6	64.2	74.7

This table indicates that the best temperature is 350°, and the proper time 6 hrs.

To further substantiate this a fusion at 350° was attempted, with other factors constant. Low and irregular yields of carvacrol resulted. The destruction of the carvacrol at 360° was considerably reduced by incorporating water in the reaction mixture. Data from this experiment are found in Table V and the graphic representation in Curve 3, Fig. 2.

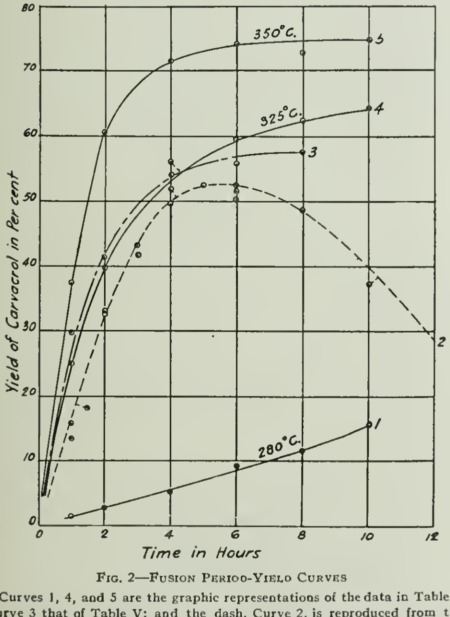

Fig. 2—Fusion Period-Yield Curves

Curves 1, 4, and 5 are the graphic representations of the data in Table I; Curve 3 that of Table V; and the dash, Curve 2, is reproduced from the work of Hixson and McKee showing the yield by the open pot fusion at 360°, 1 mole sodium cymene sulfonate to 18 moles sodium hydroxide

EFFECT OF THE AMOUNT OF SODIUM HYDROXIDE UPON THE CARVACROL YIELD—A fusion experiment was carried out using 0.1 mole sodium cymene sulfonate with various amounts of sodium hydroxide in each tube. The fusion was carried out for 6 hrs. and at 350°, that is, at the optimum fusion temperature and period as previously determined. The results obtained are recorded in Table II, and graphically in Fig. 3.

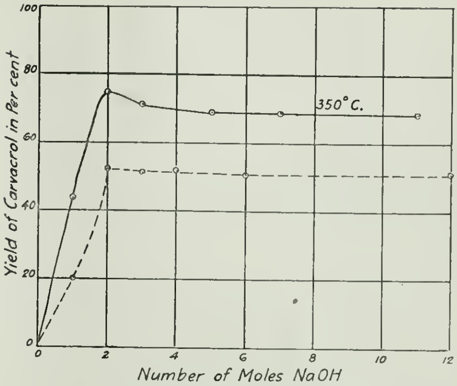

Fig. 3—Concentration-Yield Curves

The full curve plots the data found in Table II, and the dash curve is taken from the work of Hixson and McKee showing the yield by the open pot fusion at 360° for 6 hrs. with varying amounts of sodium hydroxide

Table II—Fusion Mixture

Constants—Temperature, 350°; time, 6 hrs.

Variable—Ratio of sodium p-cymene sulfonate to sodium hydroxide

Number	Number of Moles Sodium Hydroxide to 1 Mole of Salt	Carvacrol Yield Expressed as Per cent of the Theoretical
1	1	43.4
2	2	74.4
3	3	70.8
4	5	68.3
5	7	68.5
6	11	68.1

This table indicates that a slight excess over the theoretical amount of sodium hydroxide should be employed, about 2.2 moles to 1 mole of sodium p-cymene sulfonate.

EFFECT OF WATER UPON CARVACROL YIELD—Since a charge consisting only of sodium cymene sulfonate and sodium hydroxide is apt to be too viscid to pour readily even at the temperature of 350° and since in large-scale productions it is very desirable to have the fusion mixture flow readily so that the fusion kettles can be emptied without difficulty, experiments were carried out for the purpose of determining the effect of water upon the carvacrol yield. The results obtained with varying quantities of water are shown in Table III and graphically in Fig. 4.

Table III—Effect of Water

Constants—Temperature, 350°; time, 6 hrs.; 1 mole of sodium cymene sulfonate to 2.2 moles of sodium hydroxide

Variable—Amount of water

Number	Per cent Water in Charge Calculated on the Total Amount of NaOH Present	Carvacrol Yield Expressed as Per cent of the Theoretical
1	2	74.7
2	12	72.0
3	22	70.5
4	32	68.4
5	42	66.8
6	52	62.1

The data in Table III show that water in the charge tends to decrease somewhat the carvacrol yield when the fusion period is 6 hrs. Data were next obtained

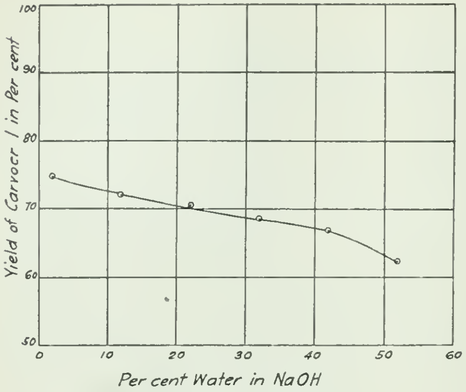

Fig. 4—Concentration of Water as Related to Carvacrol Yield. Graphic Representation of Data from Table III

to show the effect of increased time of fusion with constant amounts of water. The six tubes were filled with a mixture consisting of 0.1 mole of the sulfonate, 0.22 mole sodium hydroxide and 50 per cent water (calculated as per cent of total amount of sodium hydroxide added) and heated for varying periods of time, from 2 to 22 hrs. The results are given in Table IV and in Fig. 5.

Table IV—Time of Fusion

Constants—Temperature, 350°; 1 mole sodium cymene sulfonate to 2.2 moles sodium hydroxide and an amount of water equal to 50 per cent of the weight of the sodium hydroxide

Variable—Time

Number	Fusion Period in Hrs.	Carvacrol Yield Expressed as Per cent of the Theoretical
1	2	54.2
2	6	63.6
3	10	68.0
4	14	65.1
5	18	62.2
6	22	49.5

This table indicates that a slightly increased fusion period is necessary when the fusion mixture is diluted with water.

It is to be noted from the data of Tables III and IV and Figs. 4 and 5 that the optimum yields of carvacrol were not obtained when water was incorporated in the reaction mixture, and since experiments carried out at 360° without water in the charge showed a decided lowering of the yield, the effect of water in the mixture fused at 360° was studied. The results are recorded in Table V, and graphically in Curve 3, Fig. 2.

Table V—Fusion Period Yield

Constants—Temperature, 360°; mixture, 1 mole sodium cymene sulfonate to 2.2 moles sodium hydroxide and an amount of water equal to 50 per cent of the weight of the sodium hydroxide

Variable—Time

Number	Fusion Period in Hrs.	Carvacrol Yield Expressed as Per cent of the Theoretical
1	1	29.8
2	2	41.3
3	4	54.0
4	6	55.7
5	8	57.5

This table shows that the destruction at high temperatures is much reduced by the presence of water and that the time of fusion must be increased.

DISCUSSION OF RESULTS

From these experiments it appears that the highest yield of carvacrol is obtained when the fusion is conducted at 350° in an autoclave. When fused at this temperature with sodium hydroxide containing about 2 per cent of water, 6 hrs. seems to be the optimum fusion period. Fusions conducted for longer than 6 hrs. do not seem to affect the carvacrol yield either way. If, beside the sodium cymene sulfonate and sodium hydroxide, water is also added to the charge to the extent of 50 per cent of the sodium hydroxide used, the fusion period should be increased to 10 hrs., and under these conditions higher temperatures may be employed, thus increasing the speed of the reaction without materially affecting the yield. Small quantities of water, 10 to 20 per cent, have one beneficial effect in that the fusion mixture is more fluid, and the mass can, therefore, be readily removed from the kettle, a fact which is of considerable practical importance. So far as the sodium hydroxide is concerned, a little more than the theoretical amount should be used, 2.2 moles to 1 mole of the sodium cymene sulfonate being sufficient. More sodium hydroxide should not be used, because it is unnecessary and increases the cost of manufacturing by four factors—a reduced yield, the cost of the excess of sodium hydroxide, the cost of acid necessary to neutralize the excess and set the carvacrol free, and reduced capacity of the apparatus.

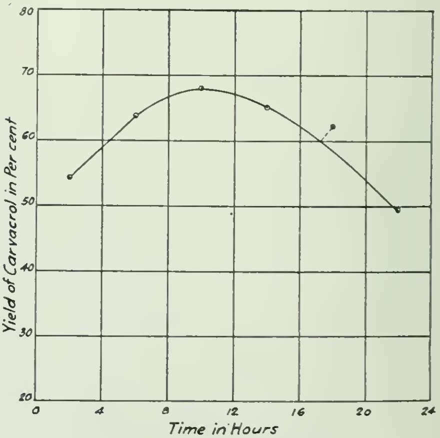

Fig. 5—Fusion Period-Yield Curve with Water in Mixture. Graphic Representation of Data in Table IV

The advantages of working in an autoclave are summarized as follows:

1—The very deleterious action of the oxygen of the air is reduced to a minimum.

2—No products distil during fusion and the reaction mixture remains constant in respect to water. A certain amount of water gives a cleaner product and permits easier emptying of the autoclave.

3—The contents of the autoclave are easily discharged through a valve at the end of the fusion, due to pressure generated within.

4—An increase of about 23 per cent in the yield is obtained by the laboratory investigations over the best laboratory yield obtained by Hixson and McKee,[1] that is, 75 per cent instead of 52 per cent. Under large-scale working conditions the presence of the necessary small amount of water in the melt may reduce the yield slightly, although it is possible that this may not be the case.

We wish to call attention to the accuracy of the method employed for determining the carvacrol in all of this work. By extracting with ether the acidified solution after fusion, a crude carvacrol is obtained that is contaminated by other extractive matter. The purity of the carvacrol extract varied from 75 to 99 per cent, and depended upon the conditions of the fusion and the care employed in drying the ether extract.

Schorger[2] weighed the ether extract and considered it as carvacrol. There is no doubt that his best yield of 52.9 per cent is for this reason too high. He employed potassium hydroxide for his open-pot laboratory fusions and states that the yields are very poor and hard to duplicate.

Hixson and McKee[1] extracted the crude carvacrol with benzene, removed the solvent by distillation and fractionated the product, taking the distillate between 227° and 245° as carvacrol; or removed the carvacrol by distillation of the acidified material with steam. Even if this material obtained by either method is further purified, as they state,[3] it seems reasonable to expect that it still contains impurities.

SUMMARY

I—An apparatus especially suited to laboratory studies of caustic fusions is described.

II—The various factors of temperature, time, and concentration affecting the fusion of sodium cymene sulfonate with sodium hydroxide have been studied, and it is shown that by conducting the fusion in an autoclave yields of carvacrol as high as 75 per cent are readily obtained, as compared with less than 60 per cent by fusion in an open pot.

III—The fusions of other sulfonic acids are being studied.

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[1] *Loc. cit.*

[2] This Journal, **10** (1918), 260.

[3] "This was done by redistilling the product obtained from the fusion liquor by either of the two methods mentioned. No difficulty was experienced in getting a product with a fairly constant boiling point."

THE USE OF HYDROGENATED OILS IN THE MANUFACTURE OF TIN PLATE

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Received August 4, 1919

The manufacture of tin plate in the United States consumes from 5,000 to 10,000 tons of palm oil per year. Many substitutes have been tried without success, and there has developed in the industry a general belief that no satisfactory substitute exists. Tallow was used in the early manufacture of tin plate, but for many years palm oil has been the only oil used in tin pots.

When shipping difficulties arose on account of the war a shortage of palm oil was threatened. With the increased demand for tin plate some pressure was brought to bear to secure the palm oil said to be essential for production. At this time attention was called to a patent[1] which covers the use of glycerides or esters of saturated fatty acids, all kinds of hydrogenated oils and fats, and artificial esters produced from palmitic acid, stearic acid, or other saturated acids. Available statements in regard to this process were not in agreement as to its practicability and economy.

The work reported in this paper was undertaken to secure definite information as to the conditions of satisfactory production of tin plate without palm oil.

PROCESS OF MANUFACTURE

To make tin plate, cleaned sheets of steel are thrust singly into a bath of molten tin, entering through a layer of zinc chloride flux which covers part of the surface of the tin bath. The sheets are carried by rolls up out of the tin through oil which floats to a depth of about 15 in. over the tin. The oil serves to prevent oxidation of the surface of the tin bath, and to dissolve tin oxide which may be formed. The temperature of the tin is around 315° C. (600° F.), and that of the oil near the surface about 240° to 250° C. It is evident that oil for this purpose must stand a high temperature without undue volatilization or decomposition. With palm oil care must be taken that the temperature does not become too high, since at higher temperatures the oil polymerizes, loses its power to keep the plate clean, and is carried out on the plate in excessive amount.

PRELIMINARY LABORATORY EXPERIMENTS

Before attempting a practical test a few experiments were made to observe the effect of heat on different oils. The vegetable oils obtained in the United States are all too volatile to be worth considering for continuous heating at 250° C. The only easily available hard oil is cottonseed oil hydrogenated to different degrees of hardness. For preliminary heating experiments there was at hand a lard substitute consisting of cottonseed oil hardened to an iodine number of 97 and some cottonseed oil hardened to an iodine number of about 19.

Lots of about 100 g. of oil were heated in porcelain crucibles which were set in holes in asbestos board over Bunsen burner flames. The temperatures were not regulated very closely and varied from 200° to 300° C. at different times.[2] Buttons of tin weighing about 50 g. and oxidized by previous heating in the air were placed in the bottoms of the crucibles. The oils were heated seven times, usually 5 or 6 hrs. at a time. The weights of oil and of tin were obtained after each heating. The tin was oxidized each time by heating in the air, and fresh oil was added to replace the loss during heating. At the end of the seventh heating the palm oil and the lard substitute had polymerized to such an extent that they would have been entirely useless in a tin pot, so they were rejected and a fresh lot of palm oil was compared with the same hard oil and another material which had been offered as an improvement over the very hard oil. This material, a by-product fat, was more like palm oil in its physical properties and enough cheaper than the hardened cottonseed oil to make it more economical if it could be used. The lots were heated eight times more, when the palm oil and the by-product fat were so polymerized as to be useless. The very hard product was still in fair condition.

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[1] U. S. Patent 1,242,532 (October 9, 1917)

[2] Temperature readings in the laboratory heating tests were taken with thermometers not wholly immersed and were not corrected. They are, therefore, all low, but comparable for the different oils.

The behavior of palm oil in the crucibles resembled its behavior in a tin pot, that is, with successive heatings it became more viscous when hot, and harder when cold; the loss from fresh oil was more rapid than after it had been heated for some time; and it brightened the oxidized tin.

The lard substitute resembled palm oil, but it polymerized somewhat more easily. The by-product fat, which contained more free fatty acids than any of the other samples, attacked the oxidized tin much more vigorously. It lost more weight than palm oil at lower temperatures, and polymerized in about the same time. The heating tests indicated, on the whole, that the lard substitute and the by-product material would not give as good service as palm oil in a tin pot.

The very hard oil did not clean up the oxidized tin well during the first few heatings, but as the heatings continued, it became softer when cold than it was when fresh, and cleaned the oxidized tin well. At first the hard oil was much more fluid than palm oil when melted, but after several heatings it became somewhat thicker when melted. It lost much less weight than palm oil during the heating.

These experiments indicated that a very hard hydrogenated cottonseed oil might be expected to stand the heating in a tin pot without any disagreeable consequences in the way of unpleasant odors, excessive loss from volatilization or from polymerization with consequent carrying out of oil on the plate leaving the bath.

COMMERCIAL TEST

In order to learn how the hardened oil would work in a tin pot, arrangements were made for an operating test. Through the kindness of Dr. David Wesson enough hardened cottonseed oil was secured to make a fairly thorough test. The first lot obtained had an iodine number of about 3. A second lot had an iodine number of about 17. This latter was the hardest oil which could be secured at the time without having a special run made, as was done for the first lot. There was no detectable difference in operation between the two lots.

The experiment was carried on at a tin plate plant which had been in operation less than a year. The equipment was therefore new and uniform throughout the plant, but had been operating long enough to be broken in and running normally. The tin pots were of the type most widely used in this country, with 84-in. rolls. The plate was cleaned by a machine of the usual type. Ground peanut hulls were used for cleaning.

At the start of the experiment all the oil was removed from one pot at the regular Saturday cleaning. Eight hundred and fifty pounds of hardened oil were added to the pot, and, on the basis of the preliminary heating experiments, the superintendent of the plant was urged to keep the oil as hot as possible over Sunday while the mill was not in operation. However, on account of unfortunate past experience with substitutes for palm oil, the foreman in charge kept the pot with hardened oil at a lower temperature than the pots with palm oil, which are normally kept much below the working temperature over Sunday.

When the plant started Sunday night very unsatisfactory plate was produced on Stack 9, where the hardened oil was in use. The plate continued poor for several turns after the other stacks began to produce satisfactory plate. It was not possible to clean the oil from the plate by one treatment, even when the pressure of the rolls in the cleaning machine was increased, and fresh peanut meal was added more often than usual. Recleaning removed all the surplus oil and gave a marketable plate, though the product of the first few turns was not up to the average quality of the plant.

The first plate made was not very bright. An average sheet selected from one of the other stacks by the manager appeared much better than an average sheet from Stack 9. Analysis of 12 samples from each of these two sheets showed an average of 1.33 lbs. of tin per base box for the sheet from Stack 9, and 1.72 for the other. Two sheets from Stack 9, taken during the second turn of its operation with hardened oil, carried 1.10 and 1.21 lbs. per base box. Five other sheets taken as representative sheets from Stack 9 during a period of 10 wks. carried 1.47, 1.33, 1.58, 1.58, and 1.55 lbs. of tin per base box.

After the first three days the plate from Stack 9 appeared to be in every way as good as the average product of the plant. At the beginning of the second week the first sheets made on all stacks in the plant were compared, and the plate made on Stack 9 was in no way different from that made on the other stacks.

The loss of oil by volatilization during the first week was much greater than the loss during subsequent weeks. The quantity added each day during any week was much less for Stack 9 than for those using palm oil.

After the first week no special attention was given to Stack 9, except to make sure that no palm oil was added. This was not difficult, as the tinners all preferred the hardened oil. It was operated with hardened oil alone for 12 wks. When the supply was used up additions of palm oil were made as required, with no effect on the operation of the machine.

The plate produced with hardened oil was not noticeably different from the rest of the plant product. Some observers thought that the front edges of the plate from Stack 9 were a little better than the average. The quantity of oil carried out on the plate appeared much less with the hardened oil.

TABLE I—LOSS OF WEIGHT ON HEATING 100 G. OF OIL FOR 5-HR. PERIODS AT THE TEMPERATURE INDICATED

Oil	Iodine Number	Loss during Each Period						Total Loss at End of Each Period					
		200°	220°	240°	260°	280°	300°	200°	220°	240°	260°	280°	300°
Palm oil	54	5.3	4.8	5.4	10.4	16.5	....	5.3	10.1	15.5	25.9	42.4	....
Hardened cottonseed oil	17	1.8	1.8	3.1	7.2	10.4	15.8	1.8	3.6	6.7	13.9	24.3	40.1
Rendered tallow	35	0.7	1.2	2.4	4.7	7.2	18.9	0.7	1.9	4.3	9.0	16.2	35.1
Unrendered tallow	32.5	2.0	1.3	2.7	1.1	5.2	11.6	2.0	3.3	6.0	7.1	12.3	23.9
By-product fat	32	11.3	16.9	15.8	5.5	9.2	7.4	11.3	28.2	44.0	49.5	58.7	66.1
Hardened herring oil	60	2.4	3.8	4.5	5.8	12.0	15.9	2.4	6.2	10.7	16.5	28.5	34.4

Although palm oil is not very disagreeable for the operator, the hardened oil was enough better in this respect to be noticeable.

The hardened oil in actual use did not show any tendency to polymerization, although at several times it was heated to temperatures much higher than would be safe with palm oil. There is also less danger of setting fire to the hardened oil when cleaning the tin pot.

There would seem to be no reason to expect economy in the consumption of tin with the use of hardened oil, unless the weight of coating on the plate should be decreased.

Six weeks after the hardened oil was used up the tin house records were examined by the superintendent of the plant and one of the authors of this paper. The production of plate and consumption of tin and oil on Stack 9 were compared with the values for the other stacks in the mill for several weeks preceding, for the 12 wks. of the test, and for the succeeding 6 wks. The following conclusions were reached: Over a considerable period Stack 9 does not differ materially from the average in performance. The tin consumption with hydrogenated oil was not appreciably different from that with palm oil. During the 12 wks. of the test the oil used per base box was not over $^3/_4$ of the average amount of palm oil used under similar conditions.

IODINE NUMBERS OF OIL SAMPLES

No extensive analyses of oil samples were made. The first and second lots of hardened oil used had iodine numbers of 3.1 and 16.7, respectively.

At the end of the first week of use the hardened oil in the tin pot had an iodine number of 17.0. Samples on successive weeks gave values of 19.6, 21.2, 24.2, 25.3, 33.4. After the sixth week the values varied between 30.5 and 35.3 for the remaining 6 wks. of the test. Beginning at the thirteenth week, when palm oil was added, samples taken for 6 wks. had iodine numbers from 50.2 to 41.0, with no regularity in the variations. At about the middle of the period of use of hardened oil samples were taken on one day from 14 pots operating with palm oil. The iodine numbers varied from 41.7 to 53.6, the average being 45.0. Iodine numbers were obtained for several samples of beef tallow which had been heated in crucibles for different lengths of time. The original tallow had an iodine number of about 32. After heating for 5 hrs. at about 200° C., 6.5 hrs. at 220° C., and 7 hrs. at 240° C., the iodine number was 24.2. Further heating for 6-hr. periods at 260°, 280°, 290°, and 300° did not produce much change in the iodine number. It was from 22.3 to 24.5 for these samples.

These results indicate that palm oil in a tin pot will have an iodine number around 45, hydrogenated cottonseed oil about 32, and tallow about 23.

HEATING TESTS

At the conclusion of the commercial test further experiments were conducted to determine losses on heating of the oils which had been used in the tin pots, together with some similar materials which were at hand. The palm oil and hardened cottonseed oil were from lots used in the experiment at the plant. Beef kidney fat, purchased at a local market, was used rendered and unrendered. The by-product fat has been described above. A sample of Alaskan herring oil which had been hydrogenated until it had an iodine number of 60 was obtained from the Oil, Fat and Wax Laboratory of the Bureau. Samples of about 100 g. of the oils were heated in crucibles for from 4 to 7 hrs. at each temperature from 200° to 300° C., inclusive, by 20° stages.

Table I shows the loss calculated on a basis of 100 g. original weight and a 5-hr. heating period at each temperature. The losses are given both for the individual periods and as total losses from the beginning of the heating to the end of each period.

The great loss of the by-product fat indicates clearly that there would be no advantage in using it when other materials were available. No values were obtained for palm oil above 280°, because at this temperature the oil polymerized to such an extent that it would be unfit for use in a tin pot. The behavior of the hardened cottonseed oil and of the palm oil is in agreement with their action in the tin pot. Tallow acts much like the hardened cottonseed oil in heating, and is said to resemble it in actual use. The chief objections to the use of tallow are said to be its unpleasant nature, as it decomposes in storage, and the greater difficulty in cleaning it from the plate, as compared with palm oil. The behavior of the hardened herring oil was very interesting. Although much softer than any of the other products except palm oil, having an iodine number of 60, it lost weight slowly on heating and showed very little tendency to polymerize on prolonged heating at 300°. It seems entirely probable that a more completely hardened oil of the nature of this sample of herring oil might prove superior to the hardened cottonseed oil for use in tin pots. It must be understood that these laboratory heating tests only indicate in a general way the probable relative losses in actual use.

SUMMARY

Laboratory heating tests give useful indications of the relative values of different oils for use in tin pots.

During 12 wks. a tin pot using hydrogenated cottonseed oil operated somewhat better than with palm oil. The consumption of hardened oil was distinctly less than the consumption of palm oil. There was no appreciable saving of tin.

If palm oil should be unobtainable for the manufacture of tin plate, it could be replaced by hydrogenated cottonseed oil with no loss in operating efficiency.

With the industry adjusted to the use of palm oil, the higher cost of hardened oils probably balances the advantage to be obtained by their use, leaving little if any margin to pay for the privilege of using the hardened oils.

Heating experiments indicate that a hydrogenated fish oil might be obtained which would be satisfactory for use in tin pots, though hardened to a less degree than is necessary for the best results with cottonseed oil.

LEAD COATED IRON[1,2]

By Charles Baskerville

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Protective coatings for the prolongation of the life of iron and steel fall into three general classes, well described in a report from the Bureau of Standards (1919) as follows:

1—Metallic coatings.

2—Coatings in which the iron to be protected is itself converted at the surface into some less corrodible compound.

3—Organic coatings (varnishes, paints, enamels, etc.).

The present paper has to do with the first of the three classes and is especially concerned with the use of lead and lead-antimony alloy as protective agents.

If the iron be completely covered by another metal its life depends upon the ability of the covering metal to withstand the corrosive action of air and water to which it may be exposed. This is materially affected by the presence of various chemical fumes and gases such as sulfur dioxide, nitrogen oxides, chlorine, sulfuric acid, alkali-mists, etc. Mechanical strains, vibrations and the rough handling which usually obtains during packing, transportation, installation, etc., may bring about ruptures and scaling in the protective coating and thus expose the iron or steel which may have been originally perfectly covered.

The best manufacturing practice seeks a perfect coating initially but experience has shown the necessity for subsequent precautions because, where two metals, which always have a potential difference, are in juxtaposition in the presence of electrolytic water (acidulated, alkaline, or saline) electrolysis sets up with corrosion of one of them. If the iron be the electropositive member of the couple, it corrodes—the corrosion being activated by the presence of the other metal. Aluminum and zinc are electropositive to iron, and therefore are theoretically the best practical metallic protective coatings for iron, where the coating is broken, as they bear the burden of corrosion. Zinc forms several alloys with iron which are also electropositive to iron in a lesser degree. Tin, lead, copper, antimony and most of their alloys are electronegative, and hence facilitate the corrosion of the iron if it is incompletely covered or exposed by abrasion or other rough treatment. Practice has shown the importance of painting sheet tin and galvanized iron to fill in the broken coating.

Since lead is the cheapest of all the metals used for coating iron, and in addition gives the covered metal certain other desirable qualities, a commercial method of application has long been sought. It is hardly justifiable to incorporate here a bibliography on the subject. The most successful of the numerous efforts in this direction is the well-known terne plate, an alloy of about 75 per cent lead and 25 per cent tin, but this involves the use of costly tin. Lead has been successfully sprayed on iron by an atomizer (Schoop process) and the process is well suited for certain detailed protective work, but it is far too expensive in expert labor and time for tonnage production.

Modern interest in electronic conceptions and in the difference in properties of metallic allotropes caused us to investigate the processes covered by United States patents granted to Goodson,[1] which, briefly, consisted in subjecting a column of molten lead of small cross section in motion to the influence of an alternating current of low voltage and high current density for several hours, it being asserted that the lead thus became "activated," the molecular distribution effecting such change in physical condition that it would attach itself so firmly to iron that when the lead solidified it would not shrink away from the iron and leave exposed surfaces. Evidence of the production of an iron-lead alloy binder did not appear. The conditions detailed in the patents were carried out most conscientiously, with such additional advice and assistance as the inventor was able to give. It is hardly necessary to describe the apparatus used. Some promising results were obtained, but on checking up with metal not treated electrically the results were virtually duplicated.

Since it seemed that the problem of successfully and economically coating iron and steel with lead was not unsolvable, investigations were prosecuted along other lines and resulted in the production of products satisfactory for some purposes.

In working out a process for using lead and lead-antimony alloys as a protective coating on sheet iron and steel, the fundamental problem was to find a binder which would tie iron and lead firmly together. After much experimentation a preliminary coating of antimony proved to serve the purpose. Melted lead shrinks materially when it solidifies. Antimony tends to overcome this shrinkage, as is well known from the conduct and composition of type metal. Moreover, the alloy formed is harder than lead. With a preliminary coating of antimony followed by dipping in lead, the latter acquires an increasing percentage of antimony. This fact, together with the other observations, caused us to use a lead-antimony dip (eutectic of 12.5 per cent antimony) in the production of "protected iron" on a technical scale. Bending, twisting and hammering tests proved that the iron foundation would break before the coating. Photomicrographs clearly disclosed the antimony binder.

About 800 shingles, 9 × 16 in., of mild steel, of 24 and 28 gauge, were made. Some of these sheets were subjected to aërated distilled water tests after having been pickled in sulfuric acid (6 : 1), washed with water, thoroughly blackened by an antimony chloride solution, again washed in water, and while still wet dipped through zinc chloride flux into molten lead-antimony (12 per cent), then into molten lead and finally quenched in oil. One series gave no iron rust indications during eleven days. In another series, aërated tap water tests brought out a few pinholes during the same period, but on the whole the condition of the samples was good. Allegheny iron, 26 gauge, showed some pinholes in both distilled and tap water aërated during 5 days. Rust usually showed first wherever there were sharp angles. In preliminary experiments many pinhole detection tests were made by the gelatin-ferricyanide method.

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[1] Presented at the 57th Meeting of the American Chemical Society, Buffalo, N. Y., April 11 to 13, 1919.

[2] Most of the experimental work described was done by Mr. V. A. Belcher.

[1] U. S. Patents 789,690; 789,215; 900,846; 900,847; 978,448; 1,061,066; other applications pending.

Two exposure tests of these shingles were made by the Research Laboratory of the National Lead Company, in Brooklyn, and are being continued. One test was with the coated shingles, packed and shipped in the same way as tin plate is, from the Maurer, N. J., plant of the United Lead Company. The other test was made with a smaller lot prepared at the same time, but painted on both sides. After an exposure to the weather for over three years, with all the varying conditions of temperature, rain, and snow of that period, both tests show 100 per cent efficiency, according to the reports from the director, Mr. G. W. Thompson. Another test was made by Mr. V. A. Belcher, on a roof in Michigan. After a considerable time the shingles were reported to be still in good condition. A test roof adjacent to a chamber sulfuric acid plant at Maurer, N. J., did not give satisfactory results. These shingles are not to be recommended, therefore, for use under the last-mentioned conditions, where considerable quantities of nitrogen oxides or sulfur dioxide may be in the air.

The weight of the protective coating was determined by cutting from shingles, test pieces presenting approximately 3 sq. in. of covered surface. After accurate measurement each piece was weighed. The metal was stripped with acid, washed, dried and again weighed. Iron, which had gone into solution by stripping, was separated and weighed as Fe_2O_3. The total iron thus determined, subtracted from the original weight of a piece, gave the amount of protective coating for the surface exposed. The average coating was 319.2 mg. per sq. in., or approximately 92 g. of coating per shingle. This was subsequently checked by weighing ten shingles before and after pickling, and before and after coating. The average proved to be 92 g. for 28 gauge and 93.5 g. for 24 gauge shingles, that is to say, 46 to 47 g. (about 1.5 oz.) per sq. ft.

Galvanized iron wire cloth was stripped with caustic soda. The wire was 23 gauge Trenton or 22 gauge B and S and corresponded to 4 mesh cloth. The amount of zinc per sq. in. averaged 438 mg. (63 g. or about 2 oz. zinc per sq. ft.). The nodules of zinc where the wires crossed varied in size. With wire gauze, 20 gauge Trenton or 19 B and S, 4 mesh, 12.5 per cent lead-antimony alloy gave 212 mg. coating per sq. in. (30 g. or about 1 oz. per sq. ft.). When first dipped in 12.5 per cent lead-antimony and afterwards in lead, the coating proved to be 270 mg. per sq. in. Cheap chicken wire and other netting may easily be coated with lead-antimony.

Several hundred feet of iron wire were coated, using an improvised outfit for moving the wire through the process. Smoothly drawn annealed wire took a good coating. Barbed wire was not successfully coated, for the points and sharp edges of the barbs were not covered, and quickly showed rust in the corrosion tests.

Extensive experiments were made in an effort to produce a satisfactory exterior coating on iron pipe to be used for petroleum pipe lines. Three-foot lengths of 8-in. pipe, some pieces being threaded at both ends, couplings for the same, and smaller pieces of 2-in. and 3-in. pipe, were used. All were obtained from the Pittsburgh plant of the American Tube Company. Suitable pickling vats, washers, antimonizers, and lead baths were devised, and a special mechanism designed and installed for dipping the pipe while in motion, the revolutions being controlled at will. Pipes were coated with lead and lead-antimony (12.5 per cent).

Corrosive experiments (aërated water tests, air exposure, burying in moist soil, etc.) showed a fairly good product, but not of sufficiently good grade to warrant production. The irregular surface of the pipe produced in milling interfered with perfect pickling and the subsequent necessary rough handling with pipe wrenches, etc., abraded the softer metal, thus exposing the iron.

At the request of the War Department, attempts were made to apply the process to produce a coating within shell to hold certain poison gases. Owing to the very irregular milled surface of the interior a perfect coating was not obtained.

The unusual recent interest in "passive" iron raised the question whether iron rendered passive might take a better coating of lead-antimony alloy. Two general methods of making iron "passive" were used; namely, treatment with aqueous solution of oxidizing agents (permanganates and dichromates) and with acid solutions. The final conclusion was that "passivity" did not improve the product.

A process was worked out for forming a binder on cast iron upon which pure lead could subsequently be cast and molded, especially for filter presses and filter frames. This involved the removal of silica (sand adhering from the mold), which prevented a uniform deposit of antimony and lead. The coating is successfully accomplished by introducing an extra step of pickling in hydrofluoric acid prior to treatment with the antimony salt solution. The coating thus produced is not sufficiently heavy and uniform to admit of practical use, but forms an excellent binder for casting thereon lead or lead alloy of any desired thickness.[1]

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[1] The process covering the treatment to secure the satisfactory binder is covered in application for U. S. Patent 847,323.

Sheet iron may be pressed into a variety of shapes without lubricants. If, however, the metal is subsequently to be plated (nickel, copper, etc.), the shaped articles (caps for automobile hubs, etc.) require pickling. Iron in sheets lends itself to pickling much more readily than when already shaped and formed. Moreover, in pressing, the scale is often forced into the metal, making pickling an even more difficult and expensive process. Lead is soft and, even though the deposit be not devoid of pinholes, serves as a lubricant in pressing. Processes have been worked out in this laboratory for plating lead-coated iron with copper or nickel or both.

SUGAR SIRUP FROM HOME-GROWN SUGAR BEETS[1]

By John M. Ort and James R. Withrow

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Sirup can be made from home-grown sugar beets for both culinary and table purposes. When made by published methods, this sirup is not always completely palatable and free from beet flavor. Experimental modifications of published processes gave a product leaving much to be desired, though it possessed no more objectionable flavor than the average sorghum sirup. The complete elimination of green portions greatly advanced the production of a highly satisfactory sirup flavor.

Interest in the subject among farmers is no new thing. Sugar beets are easily grown and a small plot would furnish the average rural household with ample sugar sirup. Beet sugar making would probably be a universal farm industry in many parts of the country if there were any simple way of consistently eliminating objectionable beet flavor from the sirup. The beets contain from 12 to 20 per cent sucrose, as high as 28 per cent having been observed. The yield of beet sugar per acre varies much, but averages from 0.8 to 1.8 tons, while sugar cane is stated to yield 4 to 5 tons per acre.

DELETERIOUS SUGAR BEET FLAVORING CONSTITUENTS

In the manufacture of sugar from beet juice most of the salts and deleterious material are left behind in the residual sirup or molasses, which is salable only as a cattle food or fertilizer. The removal of the impurities of beet sirup has been the subject of experiment ever since beet sugar manufacture began. To obtain good sugar a complicated treatment of liming, carbonation, etc., must be followed and considerable sugar is left in the molasses. The sugars are believed to be held back by the albumins, alkalies, soluble nonprotein nitrogenous matters, potash, and other salts. These probably form a large portion of the undesirable flavoring material, and it is the opinion of beet sugar men generally that the sirup itself cannot be made suitable for human food. The *Sugar Beet*, October 1906, p. 124, states: "The simple concentration of beet juice would yield a sirup of very objectionable flavor and odor. To overcome this difficulty numerous laboratory experiments have been made during the last 50 years. None of the processes proposed had the slightest practical value, for all the products obtained were absolutely worthless." In the same publication it is stated that Salisbury and Kramper suggested that maple sirup be added to give the desired flavor.

C. O. Townsend and H. C. Gore[1] describe "a simple process of making from sugar beets a palatable and nutritious table sirup with a pleasant flavor. A patent for the process was issued to the authors of this bulletin for the benefit of the public so that any one is free to use it.[2] Tests by farmers as well as by the Department have proved the process to be practicable."

The authors give very complete directions in the Bulletin emphasizing especially the following points:

1—Cutting off the crowns of beets "at the point of the lowest leaf scar." The reason assigned is "that the crown or upper part of the beet contains a large part of the salts taken from the soil in the process of growth. It is desirable to have the sirup as free as possible from these mineral salts which, if present in too large quantities, would render the sirup unpalatable."[3]

2—Scrubbing free from dirt.

3—Skimming the boiling sirup. The authors state: "This operation removes the strong beet-like flavor and leaves a wholesome and palatable product."

4—Slow boiling.

5—Avoid scorching.

Although the method was simple, many reports of failure came to Ohio farm journals. Improper topping of beets was supposed to cause the difficulty.

References to the actual constituents causing taste and odor in the beet sirup are not plentiful. Classen[4] states that "the injurious nonsugars are defined as alkalies and soluble nonprotein nitrogenous matters." Leach and Winton[5] state that "beet sugar molasses is unfit for food, due to the presence of nitrogenous bodies which give it a very unpleasant taste and smell." Ware[6] gives "albumin amides" as an occurrence in the raw juice. Reference is also made to the presence of "alkalies, ammonia, and organic bases."

Of the substances identified as constituents of sugar beets, the nitrogen derivatives are apparently not the cause of the undesirable flavor. Trimethylamine is sometimes suggested as the offensive constituent, but it does not seem to exist in the sugar beet. The fact that it results as a destructive distillation product of the molasses does not prove that other processes may lead to its formation. Betaine, which does occur, is described as sweet. Choline, whatever its taste, is toxic.

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 57th Meeting of the American Chemical Society, Buffalo, N. Y., April 7 to 11, 1919.

[1] "Sugar Beet Syrup," U. S. Dept. of Agr., *Farmers' Bulletin* **823** (1917), 2.

[2] U. S. Patent 1,155,806 (Oct. 5, 1915).

[3] See also G. L. Spencer, *Agricultural Yearbook*, **1898**, 313.

[4] "Beet Sugar Manufacture," Trans., Hall & Rolfe, 2nd Ed., p. 81, John Wiley & Sons, Inc., N. Y., 1910.

[5] "Food Inspection and Analysis," 3rd Ed., p. 570, John Wiley & Sons, Inc., N. Y.

[6] "Beet Sugar Manufacturing and Refining," 1st Ed., 1 (1905), 136, 346, J. Wiley & Sons, Inc., N. Y.

The object of the present investigation was to remove the undesirable flavor without injuring the sugar. The separation of the sugar as such would be wasteful and difficult in the kitchen or on the farm, and was not undertaken in the present work.

EXPERIMENTAL

The beets used were grown in Ohio, near Toledo. Two bushels were received in November 1918, and 4 bushels in January 1919.

Details of the various methods of experiment need not be given further than to indicate results. While keeping strictly in mind the simplicity requirements of home treatment, a few experiments were added for broader insight into the behavior of the deleterious materials.

As the work resolved itself largely into a question of flavor, the preparation of large amounts of sirup by any one process was not necessary. Three to six beets (about 5 kilos) were ordinarily enough for an experiment. Following the directions of Townsend and Gore, the well-topped, unpared but sliced beets were just covered with boiling water, the temperature of which became thereby reduced to 70° to 80° C., as stated. They were occasionally shaken and unless otherwise indicated left to soak one hour. The temperature fell to 70° C. The juice was strained through cheese-cloth, evaporated over a low fire and skimmed from time to time. The thick sirup was very sweet but with a peculiar rubber- or beet-like flavor and odor. 450 cc. of sirup were obtained.

A long series of attempts was next made to eliminate or destroy the undesirable flavor. Among them may be mentioned clarification by milk, as in the case of maple sirup; preliminary desiccation, both atmospheric and vacuum, to coagulate albumins, etc.; liming, with subsequent precipitation by $(NH_4)_2CO_3$; peeling, decoring, dialysis; and treatment with such substances as fuller's earth, tannic acid, bleaching powder, basic magnesium carbonate, Na_2SO_3, NH_4OH followed by H_3PO_4, and bone-black. Varying degrees of clarification were secured but no marked improvement in flavor. The use of Celite appeared to improve the flavor at times. Iron, like copper, left a metallic after-taste, less pronounced than when copper was used, and gave a darker sirup.

Variations of the temperature of extraction gave no improvement. A cold water extract had the same flavor as a hot one.

Experiments on the influence of the time of soaking the beets indicated that the greater part of the undesirable flavor was removed in the early part of the soaking period. The product of a 10-min. soaking was more bitter than that of the next 50 min., but the latter was not as much improved as was desirable. A process of peeling, decoring, slicing, and preliminary extraction for 10 min. gave an extract during the next 50 min. from which the peculiar flavor was not entirely eliminated, but it was not prohibitively prominent, and the sirup was light colored, nearly as bright as maple sirup, and by far the best tasting sirup produced in the early part of the investigation. Subsequent lime treatment gave a slight bitterness.

Salisbury and Kramper's method, using alum and $NaHCO_3$, gave a flavor differing from the usual one, possibly due to the alum. We agree with the authors that the product may have maple sirup added with advantage.

When samples of the sirup were boiled down, with stirring, to a white, dry, very light and fluffy powder, there appeared to be little objectionable flavor, but when dissolved in water to form a sirup, it was found to be unimproved. By aging sirup which had been sealed up while hot, good crystals of sugar could be obtained, but the bulk of the solid sugar separating had the usual beet flavor.

Toward the end of the work the beets began to soften and deteriorate from lack of proper care. It was concluded to investigate the influence of possible scorching from local superheating by direct fire evaporation. Previous work had been carried out in enamel ware dish pans. A steam-heated copper kettle was now used, treating the beets as in *Bulletin* 823. The product had a less objectionable flavor than any previous sirup made by this method and was probably as good as previous sirups made by any method. However, the after-taste of copper was left and it was ultimately concluded that, as in beet sugar manufacture, the nature of the juice renders copper vessels undesirable. To ascertain the reason for improvement in quality, a double run was made over a free flame in dish pans, using both the *Bulletin* 823 method and the method of careful decoring and peeling, which gave much better products than before with either method.

Further runs were made with both steam and flame evaporation to compare softened beets with hard beets to see if ripening processes had any part in the sudden ability to produce a good sirup, but no such distinction was found. It was noticed, however, that many of the beets had green shoulders, looking like sunburned potatoes, which develop an intensely bitter taste upon cooking. When this green portion was pared off a good sirup was produced, with but a trace of beet flavor, and even occasionally with no such flavor detectable. No extensive investigation of this point could be made on account of lack of material, but if it should be found that this method will give consistent results, it will be a simple matter to reduce the green portion by keeping the beet roots well covered with earth in the field. Sirup actually made from these green portions possessed the undesirable flavor to a very great degree, and was very dark colored. It is likely, therefore, that some, if not all, unsuccessful results bear a relation to this green portion of the beets. At sugar refineries beets are processed "as is" and no opportunity is given for selection, whereas we frequently used beets which (by accident) possessed little or no green portions. This doubtless explains the good results of Townsend and

Gore, and their failure to advise removal of the green portions.[1]

Ware calls attention[2] to the excessive amounts of albumin amides in unripe beets. Experiment showed that otherwise good sirup, if run down too far so as to really scorch, possessed an odor of urine or amines.

The color of the sirup from sugar beets was usually dark brown and turbid. Better filtration through felt or absorbent cotton, as in maple sirup production, will reduce turbidity and thereby reduce beet flavor. The beet slices after extraction rapidly became dark brown or black, as many vegetable materials do. A batch run down as rapidly as possible produced sirup many shades lighter than any previous product; in fact it was paler than many grades of maple sirup.

A single illustration of the quantitative results may be given. Seven beets were peeled and all rotten and green parts removed. The weight was 4.3 kilos. They were sliced, soaked in water as usual for an hour, the juice strained and the water extraction repeated. Results are shown as follows:

	Sirup Yield	Sp. Gr. at 15° C.	Sucrose by Sp. Gr.	Sucrose by Polariscope	Sucrose Recovered
First	325 cc.	1.400	77.5 per cent	75 per cent	252 g. (by sp. gr.)
Second	175 cc.	1.280	58.2 per cent	54 per cent	102 g. (by sp. gr.)

The sucrose by specific gravity was taken from the usual tables. The polarimeter determination was by the method described in Leach, assuming that nothing optically active was present except sucrose. From these figures 9 beets would yield $^3/_4$ lb. of sugar equivalent, or 8.2 per cent of the weight of the peeled beets.

The wastage from whole beets from paring may be as high as 20 per cent. Gore and Townsend state that 30 or 40 beets averaging from 1 to 2 lbs. make a bushel and give from 3 to 5 quarts of sirup.

It has been suggested that beet sirup might produce diarrheal effects, due to its salts, but such an effect has not been reported to us. It would appear that the salts of sorghum also have no such objectionable quality.

The statement has been made that the sirup does not keep well. In our work no attempt was made to preserve the product. Specimens which were opened but seldom remained in good condition. The sirup contains abundant material to support mold growth, and thorough sterilization is necessary. Maple sirup would also sour if it were thinner than 11 lbs. per gallon (65 per cent solids and 35 per cent water).

The cost of sugar beet sirup making will vary with the individual case. With proper care beets can be stored for months and manipulated as required, or the product made in equipment like that for maple sirup and canned for use. Maple sirup in Ohio cost 45 to 75 cents per gallon to produce before the war. Beet sugar sirup under the same conditions would probably cost about 75 cents, because of extra labor.

CONCLUSIONS

1—The various published processes for making palatable sugar beet sirup do not consistently fulfil all claims made for them.

2—The use of copper kettles in beet sirup making is undesirable since it gives a metallic after-taste to the sirup. Enamel and aluminum ware are satisfactory.

3—The process of skimming will not in itself eliminate objectionable beet flavor.

4—The peculiar flavor can be practically eliminated from sugar beet sirup by proper attention to topping, paring off green portions, and brief preliminary extraction. The entire absence of green portions is necessary to good flavor.

5—The objectionable beet flavor may be due partly to immaturity. Preliminary storage of beets in this case will improve flavor.

ACKNOWLEDGMENT

The thanks of the authors are due to Professor Vernon Davis, Ohio Director of Markets, for suggesting the problem and for furnishing beets, and to Prof. C. W. Foulk and Dean Clair Dye for suggestions.

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[1] When it was found that very unpalatable sirup was obtained by following the directions of *Bulletin* **823**, an inquiry was sent to the Department of Agriculture to ascertain the experiences of others. After this paper was read at the Buffalo meeting, a reply was received stating that varying results had been obtained. This was ascribed in some cases to the use of immature beets. It was also learned that the U. S. Dept. of Agriculture, Bureau of Plant Industry, Office of Sugar-Plant Investigations, in order to meet the difficulties encountered in following *Bulletin* **823**, now issue a mimeographed sheet calling attention to recent investigations advising additional precautions, inasmuch as air oxidation, the darkening of sliced beets, and failure to remove beet skin have "a marked effect on the color and flavor of the sirup." The statement is made that "the long continued boiling....results in an improvement of flavor," eliminating "much of the characteristic....objectionable beet-like flavor." The additional precautions recommended are:

1—Thorough ripeness of beets.

2—Peeling.

3—Immediate slicing into sufficient water to cover at least one inch to avoid darkening by air.

4—Raising temperature to 80° C., using wooden rack at bottom to avoid scorching.

Continued careful scum removal is again emphasized. The product is of the light improved quality obtained in the work herein reported. The new directions state that the sirups "possess little or none of the more or less objectionable flavor and unpleasant after-taste sometimes noted in sirups made according to the other method."

These precautions are similar to those used in the present investigation and should give better results than the original directions. No instructions are given or emphasis laid in either set of directions upon the importance of eliminating the green portion of the beet and it is probable that peeling would not entirely remove this part. The emphasis upon thorough ripeness does not cover the case, because green topped or shouldered beets may be otherwise thoroughly ripe and make good sirup if properly pared. The supplemental directions state that *Bulletin* **823** directs that: "The tops are removed, cutting them at the line of demarkation between the green and white skin," etc. No such direction was given in *Bulletin* **823**, the lowest leaf scar being the point designated, whereas on beets 12 in. long the green color on an otherwise good beet may go as low as 9 in. Such cutting would produce good sirup but waste much of the beet. In our experience the green outer part can be cut off, saving the inner part for sirup with little waste of beet.

[2] *Loc. cit.*, **1**, 348.

LIPOLYTIC ENZYMES IN OLIVE OIL

By Thos. M. Rector

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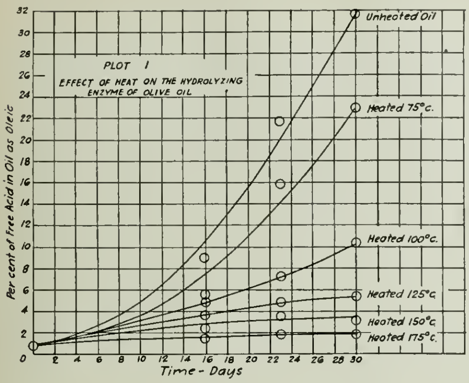
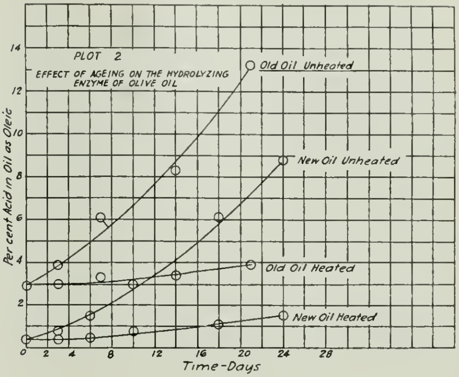
Received August 5, 1919

It has long been known that oil-bearing seed contains lipolytic enzymes which function in the germination of the seed, converting the oil into a form available as food for the young plant. The enzymes of these oil seeds, especially of castor seeds, have been extensively investigated. In fact, several commercial methods have been evolved by which oils are split into fatty acids and glycerin by means of the enzymes of castor seed and a few others of similar nature.





A fat hydrolyzing ferment, called "olease" by its discoverer, Tolomei,[1] has been isolated from olive pulp. It is claimed to be the active agent in the fermentation of the olive after crushing. Oils pressed from stored pulp or from olives that have been roughly handled often contain more than 50 per cent free acid, and for this reason olives must be pressed as soon after crushing as possible in order to obtain an oil of low acid value.

The better grades of edible olive oil come into the market without treatment other than settling and filtration. It therefore seemed possible that freshly filtered oil might contain a sufficient quantity of enzymes to produce a measurable amount of fatty acids if the oil was emulsified with water and kept at a favorable temperature. In a preliminary test such an emulsion was rapidly hydrolyzed, whereas the acidity of an emulsion of the same oil previously heated to 200° C. remained nearly constant. Further experiments were therefore made.

EXPERIMENTAL

EXPERIMENT I. EFFECT OF HEAT ON THE ENZYME.—In order to test the effect of heat on the catalytic body present in the oil, five 100 cc. portions of oil were measured into 200 cc. Erlenmeyer flasks and heated as rapidly as possible to temperatures ranging from 75° to 175° C. After remaining at the desired temperature for 15 min. the flask was cooled in a stream of cold water.

Emulsions of the heated oils were prepared in the following manner: 50 cc. portions of the oils were placed in 200 cc. Erlenmeyer flasks, 4 g. of gum tragacanth and 2 cc. of toluene were added to each flask, and the mixture shaken until free of lumps. 50 cc. of water were then added, and the flasks corked and shaken violently. By this treatment such a thick emulsion was produced that the flask could be inverted without the contents flowing out.

As a control test an emulsion was made in the same way with unheated oil. The acidity of these emulsions was determined at the beginning of the test period and at intervals during a period of 30 days, according to the customary method of determining the acid value of oils; that is, a sample of about 10 g. of the emulsion was weighed into a 300 cc. flask, 50 cc. of neutral, 95 per cent alcohol added, and the whole heated on the water bath for 30 min. The sample was then removed from the bath and titrated with $N/10$ sodium hydroxide in the usual way. In Table I the results are expressed as per cent of oleic acid in the oil phase of the emulsion (see also Plot 1).

TABLE I

		At Start	16 Days	23 Days	30 Days
Unheated	....	0.7	8.9	21.6	31.6
Heated	75° C.	0.7	5.5	15.8	22.8
Heated	100° C.	0.7	4.8	7.2	10.3
Heated	125° C.	0.7	3.6	4.8	5.3
Heated	150° C.	0.7	2.3	3.5	3.1
Heated	175° C.	0.7	1.4	1.7	1.7

EXPERIMENT 2. EFFECT OF AGE OF OIL ON ENZYMIC ACTIVITY—The oil used in the previous series of tests was about 8 mo. old. In the second experiment the enzymic activity of this oil was compared with that of oil which had been kept in a tightly corked bottle in a wooden case for a period of about nine years. Emulsions were accordingly prepared with the old oil, both heated and unheated, and the oil used in Expt. 1 heated and unheated.

TABLE II—INCREASE OF ACIDITY IN OIL WITH TIME (See Plot 2)

	At Start	3 Days	6 Days	7 Days	10 Days	14 Days	18 Days	21 Days	24 Days
Old Oil Unheated	2.9	3.9	...	6.1	...	8.3	...	13.2	...
Old Oil Heated	2.9	3.0	...	3.3	...	3.4	..	3.9	...
New Oil Unheated	0.4	0.8	1.5	...	3.0	...	6.1	...	8.8
New Oil Heated	0.4	0.4	0.5	...	0.8	...	1.1	...	1.5

Since the emulsions used in the first series of experiments were semi-solid and very difficult to handle, the formula was changed to give a less viscous mixture as follows: 100 cc. of the oil and 2 cc. of toluene were rubbed in a mortar with 3 g. of finely powdered Indian gum, a gum similar to tragacanth, until all lumps were disintegrated; 75 cc. of water were added all at once and the mixture stirred vigorously with an egg beater. A thick emulsion was formed almost instantly. This was diluted with 75 cc. of water, added a little at a time with continued stirring. By this method there was formed a freely flowing, finely divided emulsion which did not separate after a month in the incubator at 37° C.

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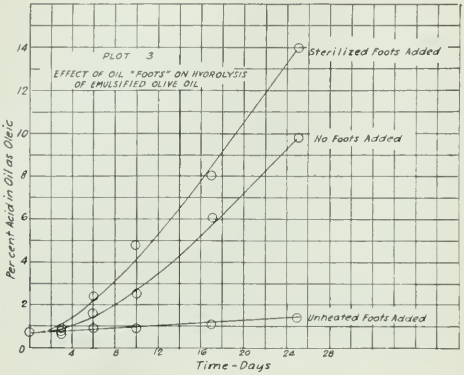
[1] *Atti. Acad. Lincei*, 1896.



EXPERIMENT 3. EFFECT OF OLIVE OIL "FOOTS" ON THE HYDROLYSIS OF OIL BY ENZYMES—It was thought probable that fat-splitting enzymes would be concentrated in the sludge settling in the bottom of the olive oil tanks, known to the trade as "foots." Accordingly some very "footy" oil was run through a Sharples centrifuge at 17,000 r. p. m. A thick, black slime was deposited in the interior of the separator bowl. This concentrated oil "foots" gave the following figures on analysis:

Water	27.40 per cent
Ash	9.27 per cent
Oil	26.79 per cent
Undetermined	36.54 per cent

50 g. of this concentrated "foots" were suspended in sufficient water to make 500 cc. This mixture was divided in two portions, one of which was heated in a steam sterilizer for 15 min. at 15 lbs. pressure. Emulsions were then made up by the same procedure as in Expt. 2, according to the following formulas:

3*a*

Olive Oil	100.0 cc.
Indian Gum	3.0 g.
Toluene	5.0 cc.
Water	150.0 cc.
Unheated "foots"	2.5 g.

3*b*

Olive Oil	100.0 cc.
Indian Gum	3.0 g.
Toluene	5.0 cc.
Water	150.0 cc.
Heated "foots"	2.5 g.

3*c*

Identical with *a* and *b* but without "foots."

It was found that in Emulsion 3*a* containing the unheated "foots" the hydrolysis of the oil was almost completely inhibited. In 3*b*, however, which contained the heated "foots" the hydrolysis ran parallel to that of the control emulsion. From this it seems apparent that the "foots" contained an anti-ferment, the effect of which is nullified by heat. The data on this series of experiments are as follows:

TABLE III—INCREASE OF ACIDITY IN OIL WITH TIME (See Plot 3)

	At Start	3 Days	6 Days	10 Days	17 Days	25 Days
Heated "foots" added	0.7	0.9	2.4	4.8	8.0	13.9
No "foots" added	0.7	0.8	1.6	3.0	6.0	8.8
Unheated "foots" added	0.7	0.7	0.9	0.9	1.1	1.4

CONCLUSIONS

The limited amount of work done in this investigation makes it unwise to attempt to draw far-reaching conclusions, but it seems justifiable to conclude:

I—That a fat hydrolyzing enzyme is contained in chemically untreated filtered olive oil.

II—That the activity of the enzyme is totally destroyed by heating the oil to temperatures around 150° C. for 15 min. and partially destroyed at 75° C. for the same period.

III—That this enzyme retains its activity for a number of years.

IV—That a lipolytic anti-ferment is contained in the aqueous phase of the water-in-oil emulsion, known as "foots."

It is hoped to extend this work to other edible oils and to a further investigation of the properties of the ferment present in olives and olive oil.

A CONVENIENT METHOD FOR THE PREPARATION OF A HYDROCHLORIC ACID SOLUTION OF CUPROUS CHLORIDE FOR USE IN GAS ANALYSIS

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Received May 26, 1919

Cuprous chloride, dissolved either in ammonium hydroxide or in hydrochloric acid, is used extensively in gas analysis for the absorption of carbon monoxide. Unless kept from contact with the air, cuprous chloride, especially in solution, changes to the stable cupric chloride, which is not an absorbent for carbon monoxide. For this reason the methods of preparing solutions of cuprous chloride for gas analysis are more or less tedious, and care is necessary to prevent oxidation.

As an absorbent for carbon monoxide in gas analysis, Winkler[1] prepares a hydrochloric acid solution of cuprous chloride as follows:

> 17 g. of finely divided copper (preferably copper powder from copper oxide reduced by hydrogen) are mixed with 86 g. of copper oxide, and the mixture is added to 1086 g. of hydrochloric acid (sp. gr. 1.124). This is tightly stoppered to exclude air and allowed to stand several days. The brown solution becomes colorless, indicating that all the copper is in the form of cuprous chloride.

Sandmeyer[2] treats 25 parts of crystallized copper sulfate and 12 parts of sodium chloride with 50 cc. of water, and heats until the copper sulfate dissolves. Sodium sulfate separates out, but is not removed. To this solution 100 parts of hydrochloric acid and 13 parts of copper turnings are added and the mixture boiled until it becomes colorless.

Frischer[3] suggests the preparation of an ammoniacal solution of cuprous salt by adding ferrous sulfate to an ammoniacal solution of copper sulfate.

Thus it appears that the presence of such compounds as ammonium chloride, sodium sulfate and ferric sulfate do not affect the efficiency of solutions of cuprous salts for the absorption of carbon monoxide.

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[1] Dennis, "Gas Analysis," p. 232.

[2] *Ber.*, **17** (1884), 1633

[3] *Chem.-Ztg.*, **32** (1908), 1005.

It is a well-known fact that cupric chloride in hydrochloric acid solution can be readily reduced to cuprous chloride by the addition of stannous chloride and this would seem a simple and effective method of making up a solution of cuprous chloride for absorption of carbon monoxide gas.

The present work was undertaken to determine whether a solution of cuprous chloride made up in this way, and so containing stannic chloride, would be as efficient for the absorption of carbon monoxide as would be a solution of cuprous chloride formed by the reduction of cupric chloride by its action on metallic copper and thus containing no other salts.

OUTLINE OF INVESTIGATION

1—The preparation of a solution of cuprous chloride, free from other salts, by the reduction of cupric chloride by metallic copper, and the determination of the acidity and copper content of this solution.

2—The preparation of a solution of cuprous chloride, equivalent to the above in its acidity and copper content, by the reduction of cupric chloride by stannous chloride.

3—A comparison of these solutions as to their efficiency for the absorption of carbon monoxide under conditions similar to those of ordinary gas analysis.

PREPARATION OF MATERIAL

CARBON MONOXIDE—The carbon monoxide used was prepared by the action of concentrated sulfuric acid on oxalic acid. The carbon dioxide and the carbon monoxide formed in this reaction were slowly passed through a train of three wash bottles of caustic potash and two wash bottles of alkaline pyrogallol to remove all carbon dioxide and oxygen. The purified carbon monoxide was then stored in a glass gasometer. Every 50 cc. of this sample were found to contain 40.2 cc. of carbon monoxide and 9.8 cc. of nitrogen.

CUPROUS CHLORIDE SOLUTION FREE FROM OTHER SALTS—Crystals of cupric chloride were dissolved in water, and enough concentrated hydrochloric acid added to hold in solution the cuprous salt which was to be formed. This solution was placed in a flask with strips of metallic copper, and heated under a reflux condenser until the reduction was well started. The solution, which will hereafter be referred to as Solution A was then placed in a well-stoppered flask and allowed to stand until colorless.

STANNOUS CHLORIDE SOLUTION—About 300 g. of metallic tin were placed in a 500-cc. flask and covered with concentrated hydrochloric acid. The mixture was heated to a slow boil, over a sand bath, for several days, and a small amount of fresh acid added from time to time until the solution was saturated with stannous chloride. The solution was then filtered and placed in a flask containing metallic tin to prevent the oxidation of the stannous chloride.

CONCENTRATION OF THE SOLUTIONS

COPPER IN SOLUTION A—One cc. of the cuprous chloride solution was oxidized to cupric chloride by the addition of dilute nitric acid and then diluted with water to 30 to 40 cc. The amount of metallic copper present was then determined by the ordinary iodometric method. An average of duplicate determinations showed that the cuprous chloride solution, Solution A, contained 0.1272 g. of metallic copper per cc.

ACIDITY OF SOLUTION A—Ten cc. of Solution A were diluted with water until the cuprous chloride was completely precipitated. The solution was then titrated with a standard solution of sodium hydroxide, using phenolphthalein as an indicator. Duplicate determinations showed the acidity to be 0.2518 g. of hydrochloric acid per cc.

ACIDITY OF STANNOUS CHLORIDE SOLUTION—The acidity of the stannous chloride solution was determined by precipitating and filtering out the tin by the addition of sodium carbonate, and titrating the filtrate with a standard solution of silver nitrate. There was found to be 0.934 g. of chlorine in every 2.5 cc. of the solution. By titrating the stannous chloride solution with a standard copper solution, 2.5 cc. were found to contain 0.934 g. of chlorine combined as $SnCl_2$. Since this amount is the same as the total amount of chlorine found to be in 2.5 cc. of the stannous chloride solution when it was titrated with silver nitrate, there was no free acid in this particular solution.

By titration it was also found that 1 g. of cupric chloride was completely reduced to cuprous chloride by 0.7 cc. of stannous chloride solution.

PREPARATION OF CUPROUS CHLORIDE SOLUTION BY REDUCTION WITH STANNOUS CHLORIDE—Jones[1] found that cuprous chloride moistened with water to form a paste or suspended in water would absorb carbon monoxide to the same extent as if it were dissolved in acid, but found that the absorption was the more rapid the greater the concentration of the acid. Because of this fact the acidity as well as the amount of metallic copper was taken into account in the preparation of a cupric chloride solution which was to be reduced to cuprous chloride by the addition of stannous chloride. This new solution was made up as nearly as possible the equivalent of Solution A, both as to acidity and amount of copper present.

Calculating on the basis of 500 cc. of Solution A, the new solution of cuprous chloride was made up as follows, and diluted to 500 cc. with water:

Cupric Chloride	134.5 cc.
Stannous Chloride Solution	94.15 cc.
Conc. Hydrochloric Acid (11.176 *N*)	308.13 cc.

This will hereafter be referred to as Solution B.

PROCEDURE

In ordinary gas analysis it is customary to use two pipettes of cuprous chloride for the absorption of carbon monoxide in order that the second pipette may absorb all traces of gas not taken up by the first solution. In order to keep as nearly as possible to actual conditions of gas analysis this plan of using two pipettes for each solution was carried out.

200 cc. of Solution A were placed in each of two Hempel double pipettes, which were designated as Solution IA and Solution IIA. The same was done with Solution B, and designated as Solution IB and Solution IIB.

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[1] *Am. Chem. J.*, **22** (1899), 287.

TABLE I

SOLUTION A

Amount of CO already absorbed........................ 0.0 cc.
Volume of gas taken.................................. 50.0 cc.

Pipette I		Pipette II	
Time Min.	Amt. CO Absorbed	Time Min.	Amt. CO Absorbed
1	40.0	1	0.0
2	1.0	2	0.0
3	0.0	3	0.0

Amount of CO already absorbed........................ 368.7 cc.
Volume of gas taken.................................. 50.2 cc.

Pipette I		Pipette II	
Time Min.	Amt. CO Absorbed	Time Min.	Amt. CO Absorbed
1	39.8	1	0.0
2	0.4	2	0.0
3	0.2	3	0.0

Amount of CO already absorbed........................ 769.1 cc.
Volume of gas taken.................................. 50.4 cc.

Pipette I		Pipette II	
Time Min.	Amt. CO Absorbed	Time Min.	Amt. CO Absorbed
1	38.8	1	0.6
2	0.9	2	0.0
3	0.2	3	0.0

Amount of CO already absorbed........................ 1159.9 cc.
Volume of gas taken.................................. 50.2 cc.

Pipette I		Pipette II	
Time Min.	Amt. CO Absorbed	Time Min.	Amt. CO Absorbed
1	37.6	1	1.2
2	0.6	2	0.6
3	0.0	3	0.0

Amount of CO already absorbed........................ 1490.5 cc.
Volume of gas taken.................................. 50.2 cc.

Pipette I		Pipette II	
Time Min.	Amt CO Absorbed	Time Min.	Amt. CO Absorbed
1	35.2	1	3.4
2	0.6	2	0.4
3	0.0	3	0.0

SOLUTION B

Amount of CO already absorbed........................ 0.0 cc.
Volume of gas taken.................................. 50.2 cc.

Pipette I		Pipette II	
Time Min.	Amt. CO Absorbed	Time Min.	Amt. CO Absorbed
1	39.6	1	0.0
2	0.6	2	0.0
3	0.6	3	0.0

Amount of CO already absorbed........................ 365.5 cc.
Volume of gas taken.................................. 50.2 cc.

Pipette I		Pipette II	
Time Min.	Amt. CO Absorbed	Time Min.	Amt. CO Absorbed
1	39.0	1	0.4
2	0.6	2	0.2
3	0.2	3	0.0

Amount of CO already absorbed........................ 764.5 cc.
Volume of gas taken.................................. 50.0 cc.

Pipette I		Pipette II	
Time Min.	Amt. CO Absorbed	Time Min.	Amt. CO Absorbed
1	38.6	1	1.0
2	0.6	2	0.0
3	0.1	3	0.0

Amount of CO already absorbed........................ 1156.0 cc.
Volume of gas taken.................................. 50.2 cc.

Pipette I		Pipette II	
Time Min.	Amt. CO Absorbed	Time Min.	Amt. CO Absorbed
1	37.6	1	1.6
2	0.8	2	0.2
3	0.0	3	0.0

Amount of CO already absorbed........................ 1499.7 cc.
Volume of gas taken.................................. 50.2 cc.

Pipette I		Pipette II	
Time Min.	Amt. CO Absorbed	Time Min.	Amt. CO Absorbed
1	37.6	1	2.2
2	0.0	2	0.4
3	0.0	3	0.0

A sample of 50 cc. of the carbon monoxide and nitrogen mixture was transferred from a burette to Pipette I containing the cuprous chloride solution, shaken for one minute and then run back into the burette and measured to note the amount of absorption. This was repeated for a second, third, and fourth minute. The unabsorbed residue of gas was then transferred to Pipette II and the amount absorbed by the fresher solution noted for each minute.

This procedure was repeated with successive samples of 50 cc. each until about 1500 cc. of carbon monoxide had been absorbed by the 200 cc. of cuprous chloride solution in Pipette I, and the solution showed signs of becoming so saturated with carbon monoxide that it no longer gave efficient absorption. The results are given in Table I in a somewhat condensed form, but in enough detail to show a complete comparison between Solutions A and B as to their absorbing power for carbon monoxide. The data given include the results of the absorption of every tenth sample. In no case did any further absorption take place after the third minute.

Table I shows clearly that the two solutions of cuprous chloride have the same capacity for the absorption of carbon monoxide, both as to speed and completeness of absorption.

Jones[1] found that the compound between cuprous chloride and carbon monoxide was so unstable that if a solution of cuprous chloride was saturated with carbon monoxide and then heated to 60° or 70° C., exactly the same amount of gas was given off as was originally absorbed, and that as soon as the cuprous chloride solution was cooled the gas could be reabsorbed.

The following experiments were made in order to throw some light on whether or not this fact can be used to advantage in gas analysis. That is to say, can a solution of cuprous chloride saturated with carbon monoxide be freed from this gas by heating, and then have an absorption efficiency equal to that which it had originally?

Solutions IA and IB, which had previously absorbed about 1500 cc. of carbon monoxide each, were transferred from their respective pipettes to separate flasks and heated to 60°–70° C. for several hours over water baths under reflux condensers in order to drive off the carbon monoxide gas absorbed, and were then returned to their pipettes. A new sample of gas had to be made, and this contained a greater percentage of carbon monoxide than the first mixture; namely, 50 cc. of gas contained 48.4 cc. CO and 1.6 cc. of nitrogen.

Solutions IA and IB were tested as before, by running 50 cc. of the prepared gas into each pipette and taking observations as to the amount of gas absorbed each minute for 4 min.

The data given in Table II include only the results of every fifth sample, beginning with the absorption of the first 50 cc. of gas in the renewed solutions.

A comparison of results in Tables I and II would at first seem to indicate that the solutions were more efficient after renewal. In Table I, after about 900 cc. of carbon monoxide had been absorbed, Pipette I of each solution was capable of taking up 39 cc. of a possible 40.2 cc. of carbon monoxide. In Table II the same solution was able to absorb the carbon monoxide almost completely after having already absorbed over 900 cc.

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[1] *Loc. cit.*

TABLE II

SOLUTION A

Amount of CO already absorbed............ 0.0 cc.
Volume of gas taken..... 50.0 cc.

Time Min.	Amt. CO Absorbed
1	48.0
2	0.4
3	0.2

Amount of CO already absorbed........... 433.2 cc.
Volume of gas taken.... 50.0 cc.

Time Min.	Amt. CO Absorbed
1	47.8
2	0.6
3	0.0

Amount of CO already absorbed........... 912.4 cc.
Volume of gas taken.... 50.0 cc.

Time Min.	Amt. CO Absorbed
1	47.4
2	0.4
3	0.4

SOLUTION B

Amount of CO already absorbed............ 0.0 cc.
Volume of gas taken..... 50.0 cc.

Time Min.	Amt. CO Absorbed
1	47.4
2	0.6
3	0.4

Amount of CO already absorbed........... 433.6 cc.
Volume of gas taken.... 50.0 cc.

Time Min.	Amt. CO Absorbed
1	48.0
2	0.2
3	0.0

Amount of CO already absorbed........... 912.4 cc.
Volume of gas taken ... 50.0 cc.

Time Min.	Amt. CO Absorbed
1	47.6
2	0.2
3	0.4

R. P. Anderson[1] states that the rapidity with which a solution absorbs a relatively pure gas is much greater than that with which it absorbs a gas from a mixture.

This fact undoubtedly explains why Solutions A and B seem to be more efficient after renewal. The gas which was run into the renewed solutions was more nearly pure carbon monoxide than the gas used with the fresh solutions, and hence the greater speed with which the second sample of gas was absorbed.

Since this second series of tests was otherwise run under practically the same conditions as in the first series, it is evident that solutions of cuprous chloride which have been saturated with carbon monoxide may be renewed by driving off the carbon monoxide by heating, and the solution made as efficient for the absorption of carbon monoxide as it was originally.

CONCLUSIONS

I—The presence of stannic and stannous chlorides, even in relatively large amounts, in a hydrochloric acid solution of cuprous chloride, does not impair the efficiency of the solution for the absorption of carbon monoxide.

II—A practical and efficient method for the preparation of a solution of cuprous chloride for absorbing carbon monoxide consists in dissolving cupric chloride in concentrated hydrochloric acid and reducing to cuprous chloride by the addition of stannous chloride. If a slight excess of stannous chloride is added the solution may be transferred from one container to another and the pipette filled without oxidation of the cuprous chloride.

III—A hydrochloric acid solution of cuprous chloride, when saturated with carbon monoxide, may be renewed by heating to 60° and 70° C. to drive off the carbon monoxide. A solution treated in this manner will be as efficient for the absorption of carbon monoxide as it was originally, and if in renewing the solution in this way a small amount of the copper is oxidized, and the solution is not colorless, a few drops of a concentrated stannous chloride solution will again reduce it.

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[1] THIS JOURNAL, 7 (1915), 587.

THE DETERMINATION OF OXYGEN BY THE COPPER-AMMONIA-AMMONIUM CHLORIDE REAGENT

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Received June 26, 1919

Hempel[1] described a reagent for the determination of oxygen which consists of spirals of metallic copper covered with a solution which consists of a mixture of equal parts of saturated ammonium carbonate solution and ammonia of specific gravity 0.93. He states that such a solution has a vapor tension which may be neglected in most cases, and that it will absorb twenty-four times its volume of oxygen. Dennis[2] repeats Hempel's account of this reagent practically word for word. No investigation seems to have been made since Hempel's original statement.

It seemed to the writer that a different concentration of reagent might be desirable, and that other ammonium salts might be substituted for the carbonate. In determining the capacity of this reagent, the conception of Anderson[3] of the specific absorption of a gas reagent was followed. The reagent was used to determine oxygen in air, and attempts were made to determine the point at which this reagent no longer gave quantitative results on air after 5 minutes' shaking. All the analyses were made over water and the value of 20.9 per cent oxygen was adopted with an allowable error of ±0.1 per cent. The apparatus employed is illustrated in Fig. 1. A and B form a standard Hempel pipette for solid reagents. The additional bulb C and the leveling bulb D were filled with mercury which acted as a seal to prevent access of oxygen to the reagent. E is a Hempel burette modified[4] by attaching a three-way stopcock to the top instead of the ordinary two-way stopcock. The manipulation was as follows: The bulb A was filled with spirals of clean copper wire, and the whole apparatus was flushed out with nitrogen. A definite quantity of the solution to be investigated was introduced through Stopcock 1. This was forced over into A and up into the capillary just to Stopcock 2. By means of the funnel and Stopcock 3, the whole of the apparatus between Stopcocks 2 and 4 was filled with water. In the burette was measured a 100-cc. sample of air, and in passing it over into A the water in the capillary connections was forced out through the third way of Stopcock 2, thus preventing any dilution of the reagent. With the three-way stopcocks as shown, the volume of the capillary was entirely eliminated and, therefore, a capillary of rather large bore was used, making the manipulation more rapid. The sample of air was shaken for 5 min. with the reagent, and on returning it to the burette, the reagent was allowed to rise in the capillary only up to Stopcock 2. Water was then introduced through the third way of Stopcock 2 to finish flushing the gas through the capillary connection into the burette.

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[1] "Gasanalytische Methoden," 1900 Edition, p. 142.

[2] "Gas Analysis," **1913**, p. 166.

[3] THIS JOURNAL, 7 (1915), 575.

[4] White and Campbell, *J. Am. Chem. Soc.*, 27 (1905), 734.

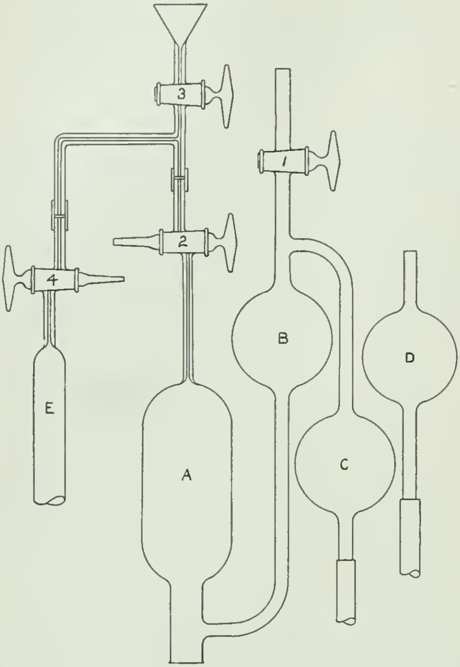

Fig. 1

Since the capacity of the reagent for oxygen proved to be so large that it would require many hundreds of samples of air, a large receiver filled with commercial oxygen was substituted at intervals for the burette E and 500 or 1000 cc. at a time introduced into A.

Table I—Hempel's Solution

Equal parts NH_4OH, sp. gr. 0.93, and saturated $(NH_4)_2CO_3$ soln., 220 cc.

Oxygen Taken Cc.	Total Oxygen in Soln. Cc.	Oxygen in Air Per cent	Carbon Dioxide Cc.	Ammonia Cc.
20.9	20.9	19.0	1.5	...
20.7	41.6	20.3	1.0	1.4
20.9	62.5	21.0	2.5	...
20.8	83.3	...	1.6	...
20.8	104.1	20.7	1.6	...
20.8	124.9	20.8	1.5	...
2069.0	2193.9	...	...	...
20.3	2214.2	17.4	2.2	0.2
20.7	2234.9	20.0	0.8	0.0
20.7	2255.6	20.5	0.3	0.0
20.7	2276.3	20.2	0.0	0.0
20.7	2297.0	20.7	0.6	0.5
20.5	2317.5	20.6	0.7	0.2
20.9	2338.4	20.6	0.6	0.0
20.5	2358.9	20.4	0.2	0.0
98.8	2457.9	...	...	...
20.3	2478.0	20.4	0.2	0.0
98.4	2576.4	...	...	...
20.9	2597.3	20.8	0.1	0.3
98.2	2695.5	...	...	...
20.7	2716.2	20.6	0.2	0.0
97.6	2813.8	...	...	...
99.2	2913.0	...	...	...
20.9	2933.9	20.7	0.2	0.7
20.7	2954.6	20.3	0.1	0.1
98.0	3052.6	...	...	...
20.3	3072.9	20.5	0.0	0.4
98.0	3170.9	...	...	...
20.9	3191.8	20.8	0.3	0.1
196.6	3388.4	...	...	...
20.5	3408.9	20.8	0.0	0.7
292.6	3701.5	...	...	...
20.6	3722.1	20.9	0.8	0.0
185.5	3907.6	...	...	...
20.7	3928.3	19.8	0.1	0.7
20.6	3848.9	19.9	0.8	0.0

The residual impurities were, of course, measured and allowed for in the calculations. Oxygen was thus introduced and, at frequent intervals, analyses of air made until the reagent either became so foul that the gas could no longer be handled quantitatively or until it failed to give 20.9 per cent in 5 min.

The first reagent experimented with was the one described by Hempel, namely, a mixture of one part of a saturated solution of commercial ammonium carbonate with one part of ammonia, sp. gr. 0.93. This reagent seldom gave 20.9 per cent of oxygen in air. It was found necessary to treat the nitrogen returned to burette E after an analysis, first with a caustic solution to remove the carbon dioxide, and then with a dilute sulfuric acid solution to remove the ammonia. The amount of ammonia reported by this manipulation naturally varied since considerable ammonia was dissolved by the burette water, and consequently the amount reported depends upon the rapidity of manipulation. Table I gives the results with the Hempel solution. It is evident that this solution will not give satisfactory results for the determination of oxygen.

Various ammonium salts were investigated, but preliminary experiments showed that ammonium chloride would possess the largest capacity and give the most satisfactory results. The following solutions were investigated:

SOLUTION 1—Concentrated ammonia, sp. gr. 0.90, saturated with ammonium chloride (see Table II). It is evident that this reagent is exhausted at about 5500 cc. of oxygen, giving a specific absorption of about 22.5 volumes.

Table II—200 Cc. of Solution 1

Oxygen Taken Cc.	Total Oxygen in Soln. Cc.	Oxygen in Air Per cent	Ammonia Cc.	Remarks
20.9	20.9	20.9	7.8	
20.8	41.7	20.8	30.5	
10.5	52.2	21.0	3.4	
10.4	62.6	20.8	2.6	
10.4	73.0	20.8	8.4	
968.2	1041.2	..	..	
20.9	1062.1	21.0	8.7	
20.9	1083.0	20.9	18.3	
10.4	1093.4	20.8	2.0	
970.9	2064.3	..	..	
10.6	2074.9	20.8	7.8	
10.9	2085.8	20.9	4.6	
971.2	3057.0	..	..	
18.2	3075.2	20.9	5.6	
20.9	3096.1	20.9	2.4	
16.7	3112.8	20.9	5.6	
968.1	4080.9	..	..	At about 3600 cc. of oxygen a precipitate of cuprous oxide began to form
16.7	4097.6	20.9	7.3	
16.7	4114.3	20.9	3.4	
16.7	4131.0	21.0	3.6	
16.8	4147.8	20.9	4.0	
483.7	4631.5	..	..	
16.7	4648.2	20.9	0.7	
16.7	4664.9	20.9	0.4	
481.9	5146.8	..	..	
16.9	5163.7	20.9	2.5	
15.5	5180.2	20.9	4.0	
481.8	5662.0	..	..	
16.3	5678.3	20.5	1.6	
16.3	5678.3	20.5	1.6	
16.6	5694.9	20.7	3.2	
483.9	6178.8	..	..	Solution absorbs oxygen more rapidly after standing over night
16.7	6195.5	20.9	3.3	
16.5	6212.0	20.7	5.6	
16.6	6228.6	20.8	5.6	
480.8	6709.4	..	..	
16.5	6725.9	20.4	1.9	
16.7	6742.6	20.5	3.8	
17.0	6759.6	21.0	3.2	10 min.
16.9	6776.5	20.9	4.8	10 min.
483.4	7259.9	..	..	
16.1	7276.0	20.2	3.9	
16.7	7279.7	20.9	3.3	10 min.

SOLUTION 2—Two parts concentrated ammonia, one part water, the mixture saturated with ammonium chloride (see Table III). The limit in this particular case is about 9500 cc. of oxygen, although this is not due to a failure to react but to the precipitate slowing down the reaction until it takes longer than the 5 min. arbitrarily set. This would give a specific absorption of 45 to 47 volumes.

TABLE III—200 CC. OF SOLUTION 2

Oxygen Taken Cc.	Total Oxygen in Soln. Cc.	Oxygen in Air Per cent	Ammonia Cc.	REMARKS
20.5	20.5	20.9	1.0	
20.7	41.2	20.8	1.4	
953.9	995.1	..	...	
20.9	1016.0	20.9	4.8	
970.2	1986.2	..	...	
19.6	2005.8	20.9	2.8	
969.3	2975.1	..	...	
19.6	2994.7	20.9	1.8	
978.0	3972.7	..	...	7 min. for absorption
978.0	4950.7	..	...	6.5 min.
978.0	5928.7	..	...	6 min. precipitate began to form
975.2	6903.9	..	...	7 min.
20.9	6924.8	20.9	0.5	
977.5	7902.3	..	...	12 min.
978.0	8880.0	..	...	20 min.
20.9	8901.2	20.9	0.2	Copper heavily coated with precipitate
977.0	9878.2	..	...	35 min.
20.9	9898.4	20.2	0.2	
20.9	9919.3	20.9	...	10 min.

SOLUTION 3—One part concentrated ammonia, one part water, the mixture saturated with ammonium chloride (see Table IV). The limit of this reagent came at the point where the precipitate was so bulky as to clog the capillaries or entrap bubbles of oxygen in the pipette. Otherwise the reaction was still quantitative. The limit is somewhere between 11000 and 12000 cc. of oxygen, giving a specific absorption of 55 to 60 volumes.

TABLE IV—200 CC. OF SOLUTION 3

Oxygen Taken Cc.	Total Oxygen in Soln. Cc.	Oxygen in Air Per cent	Ammonia Cc.	REMARKS
965.6	965.6	..	...	18 min.
21.0	986.6	21.0	3.8	
964.8	1951.4	..	...	12 min.
20.9	1972.3	20.9	3.0	
965.2	2937.5	..	...	10 min.
20.9	2958.4	20.9	1.9	
966.1	3924.5	..	...	10 min.
20.9	3945.4	20.9	1.6	
977.5	4922.9	..	...	10 min. precipitate beginning to form on coils
20.9	4943.8	20.9	1.6	
977.7	5921.5	..	...	6.5 min.
20.9	5942.4	20.9	0.1	
977.3	5919.7	..	...	8.5 min.
20.9	6940.6	20.9	0.1	
978.0	7918.6	..	...	8.5 min.
21.0	7939.6	21.0	None	
977.0	8916.6	..	...	12 min.
20.9	8937.5	20.9	None	
977.0	9914.5	..	...	15 min.
20.9	9935.4	20.9	None	
978.0	10913.4	..	...	35 min.
20.9	10934.3	20.9	None	
964.0	11898.3	..	...	45 min.
20.9	11919.2	20.9	None	Precipitate very heavy on coils and in solution. At this point capillary became clogged

SOLUTION 4—One part of concentrated ammonia, two parts water, the mixture saturated with ammonium chloride (see Table V). Here the limit was somewhere above 6000 cc. of oxygen, giving a specific absorption of 30 volumes.

The figures in Tables II to V showing the amount of ammonia given off were determined by passing the gas residue left after the analysis of air into a sulfuric acid pipette and noting the decrease. These figures are fairly reliable because, by this time, so many analyses had been run that the manipulation was very uniform.

In spite of the fact that during the earlier part of its use considerable quantities of ammonia are liberated, it would seem that Solution 3 represents the most desirable composition. Some tests have been made which indicated that in these solutions, after considerable copper has been dissolved, the absorption of acetylene is as rapid and as complete as the absorption of oxygen; and much more rapid than any of the other reagents for acetylene noted in the literature. Systematic investigation of this point has not been made.

Van Brunt[1] says that in the use of this reagent, a considerable amount of oxygen is absorbed by the cuprous salts in solution. The present set of experiments and some four years' experience with this reagent in large classes in gas analysis have shown that this is not true. Even with reagents containing large amounts of cuprous salt in solution, if the copper in the absorption pipette falls below the surface of the liquid, absorption of oxygen almost completely stops.

TABLE V—200 CC. OF SOLUTION 4

Oxygen Taken Cc.	Total Oxygen in Soln. Cc.	Oxygen in Air Per cent	Ammonia Cc.	REMARKS
975.0	975.0	..	...	30 min.
974.8	1949.8	..	...	12 min.
20.9	1970.7	20.9	None	
974.9	2945.6	..	...	10 min.
974.8	3920.4	..	...	8 min. precipitate began to form
974.7	4895.1	..	...	10 min. precipitate very heavy; trouble with capillary
20.9	4916.0	20.9	None	
975.0	5891.0	..	...	14 min. copper heavily coated and solution foaming badly
20.9	5911.9	20.9	None	
974.5	6886.4	..	...	25 min.
20.9	6906.6	20.9	None	
20.9	6927.5	20.5 20.9	None	5 min. shaking 10 min. shaking

In the analysis of commercial oxygen, where the residue of unabsorbed gas is very small, care must be taken that one or two copper wires project clear up into the entrance to the capillary; for if the gas residue is not in contact with metallic copper, the last traces of oxygen will not be absorbed. It would seem, then, that the mechanism of the reaction is that the copper is first oxidized, and the function of the solution is simply to dissolve this oxide, leaving fresh and active copper surfaces for further oxidation.

CONCLUSION

I—The solution of ammonia and ammonium carbonate recommended by Hempel and copied by Dennis is not a satisfactory reagent for oxygen.

II—The most convenient solution is made by saturating with ammonium chloride a mixture of one part concentrated ammonia and one part water. This solution will absorb from fifty to sixty times its volume of oxygen, and then fails, not by refusing to absorb quantitatively, but by the formation of so heavy a precipitate that it becomes unmanageable. The reagent is still useful for a considerable time after the precipitate begins to form.

III—The advantages of this reagent are: that it is cleaner to use and has a longer life than pyrogallate;

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[1] *J. Am. Chem. Soc.*, **36** (1914), 144.

it is free from the danger and the influence of catalyzers which interfere with phosphorus; it is readily prepared from common reagents; and it is active at almost any temperature.

IV—Its disadvantages are that it cannot be used on gas mixtures which contain either carbon monoxide or acetylene; and when fresh, it leaves measurable amounts of ammonia in the gas. This last may be remedied by keeping the burette water slightly acid.

ACKNOWLEDGMENT

The writer wishes to express his appreciation of the work of Mr. Wyatt A. Miller, who made the analyses on Hempel's solution, and to Mr. E. O. Scott, who did all the rest of the analytical work.

EQUILIBRIA IN SOLUTIONS CONTAINING MIXTURES OF SALTS. II—THE SYSTEM WATER AND THE CHLORIDES AND SULFATES OF SODIUM AND MAGNESIUM AT 25°

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Received June 6, 1919

INTRODUCTION

The equilibria which exist in aqueous solutions containing chlorides and sulfates of sodium and magnesium were discussed by Hildebrand[1] who prepared the phase-rule diagram representing the system at 25° based upon data from a number of sources, but owing to the incompleteness of these data two of the important points on his diagram were conjectural only. In attempting to ascertain by actual experiment the location of these points it became evident that some of the results used in the preparation of the diagram were incorrect, and since the diagram is of immediate importance in discussing methods for the recovery of magnesium salts from bittern and from the waters of certain lakes, it was thought desirable to redetermine all the data needed for the construction of the complete diagram. In carrying out the experimental work needed to obtain these data I have received much valuable assistance from Miss Carolyn Steel.

EXPERIMENTAL METHODS USED

This system forms a reciprocal salt pair, which can be represented graphically by reference to two axes intersecting at right angles, provided the concentrations are expressed in double equivalents per unit weight of water, that is, by using one axis to represent the relative proportions of $MgSO_4$ and Na_2Cl_2, and the other of Na_2SO_4 and $MgCl_2$. The previous work on the subject indicates that the solid phases to be expected at this temperature are $MgSO_4.7H_2O$, $MgSO_4.6H_2O$, $MgSO_4.H_2O$, $Na_2SO_4.10H_2O$, Na_2SO_4, $MgCl_2.6H_2O$, NaCl and the double sulfate $MgSO_4.Na_2SO_4.4H_2O$ known as astracanite. The problem presented was to determine the limits of the fields representing the composition of all the solutions which can be in equilibrium with each of the eight solid phases. Since the system can be expressed in terms of three components, and since a liquid phase is always assumed to be present and the pressure is constant, it would be impossible to prepare solutions which are in equilibrium with more than three of these solids simultaneously, unless the transition temperature had been chosen fortuitously, in which case four solids might be present.

In ascertaining the limits of the eight fields the following procedure was adopted: First, the compositions of solutions saturated with respect to the four simple salts $MgSO_4.7H_2O$, $Na_2SO_4.10H_2O$, $MgCl_2.6H_2O$ and NaCl were determined, and the ends of the two axes already referred to were fixed. Second, the solubility of each of these four salts in solutions containing increasing concentrations of a second salt which yielded a common ion, and, therefore, contained three ions, was determined up to the point at which a second solid phase appeared; this fixed a number of points lying between the extremities of the two axes representing solutions in equilibrium with two solid phases. Third, starting with solutions saturated with respect to two solids, the composition of solutions saturated with respect to each pair of solids in the presence of increasing concentrations of that salt which yielded a fourth ion was ascertained up to the point at which a third solid was separated.

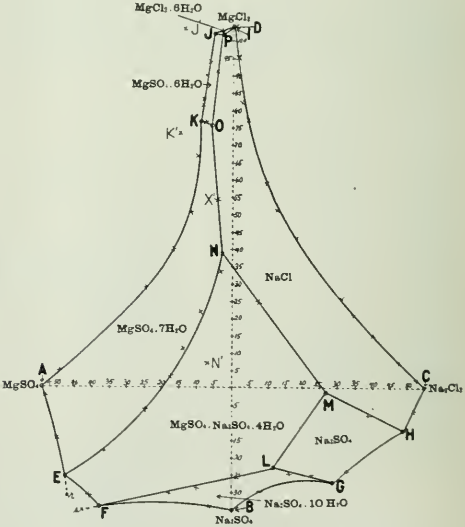

Fig. 1—The System $MgSO_4$–NaCl at 25°

This procedure made it possible to check each step in the process of establishing the critical points of the diagram, and gave more detailed information regarding the exact form of the different fields than is usually shown on similar diagrams. The details of procedure adopted in carrying out the solubility determinations differed in no essential respect from those used in similar work on the sulfates and chlorides of sodium and potassium already reported.[1]

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[1] This Journal, 10 (1918), 96.

REPRESENTATION OF THE RESULTS OBTAINED

All the data obtained, and the complete diagram which is based upon it, are represented in Fig. 1, in which the horizontal axis is used to represent the relative number of moles of $MgSO_4$ and Na_2Cl_2 and the vertical axis the relative number of moles of $MgCl_2$ and Na_2SO_4 per 1000 mols of water. The composition of each of the saturated solutions prepared and analyzed is represented by a cross, and when two or more solutions saturated with respect to the same solids were prepared the mean value of the results obtained is shown by a dot surrounded by a circle. It is obvious that all points on the diagram, except those on the peripheral lines, represent relative values only, and the actual composition of such solutions cannot be deduced from the diagram unless the total number of moles present is also known. For this reason the composition of all those solutions which represent critical points on the diagram is given in Tables I and II.

TABLE I—COMPOSITION IN MOLES PER 1000 MOLES OF WATER, OF SOLUTIONS SATURATED AT 25°

	Saturated with	$MgSO_4$	Na_2SO_4	Na_2Cl_2	$MgCl_2$	Sum
A	$MgSO_4.7H_2O$	54.36	...	...	..	54.36
B	$Na_2SO_4.10H_2O$	...	35.41	...	..	35.41
C	NaCl	...	...	54.90	..	54.90
D	$MgCl_2.6H_2O$	...	...	...	103.90	103.90
E	$MgSO_4.7H_2O$ and astracanite	47.99	24.97	...	..	72.96
F	$Na_2SO_4.10H_2O$ and astracanite	37.96	34.36	...	..	72.32
G	$Na_2SO_4.10H_2O$ and Na_2SO_4	...	27.50	29.00	...	56.50
H	Na_2SO_4 and NaCl	...	12.44	49.56	..	62.00
I	NaCl and $MgCl_2.6H_2O$	...	...	...	103.90	103.90
J	$MgCl_2.6H_2O$ and $MgSO_4.6H_2O$	5.40	...	...	102.10	107.50
K	$MgSO_4.6H_2O$ and $MgSO_4.7H_2O$	9.53	...	...	77.00	86.53
L	$Na_2SO_4.10H_2O$, $NaSO_4$ and astracanite	11.54	23.67	23.89	..	59.10
M	Na_2SO_4, NaCl and astracanite	18.84	1.28	45.72	..	65.84
N	$MgSO_4.7H_2O$, NaCl and astracanite	18.00	...	15.08	38.71	71.79
O	$MgSO_4.7H_2O$, $MgSO_4.6H_2O$ and NaCl	9.78	...	3.39	75.50	88.67
P	$MgSO_4.6H_2O$, NaCl and $MgCl_2.6H_2O$	3.78	...	0.28	101.85	105.91

TABLE II—COMPOSITION IN GRAMS PER 100 GRAMS OF WATER, OF SOLUTIONS SATURATED AT 25°

	Saturated with	$MgSO_4$	Na_2SO_4	NaCl	$MgCl_2$
A	$MgSO_4.7H_2O$	36.39	...	...	...
B	$Na_2SO_4.10H_2O$	...	27.93	...	...
C	NaCl	...	...	35.63	...
D	$MgCl_2.6H_2O$	...	...	...	54.97
E	$MgSO_4.7H_2O$ and astracanite	32.07	19.68	...	...
F	$Na_2SO_4.10H_2O$ and astracanite	25.36	27.09	...	...
G	$Na_2SO_4.10H_2O$ and Na_2SO_4	...	21.68	18.82	...
H	Na_2SO_4 and NaCl	...	9.81	32.16	...
I	NaCl and $MgCl_2.6H_2O$	...	...	...	54.87
J	$MgCl_2.6H_2O$ and $MgSO_4.6H_2O$	3.61	...	...	54.01
K	$MgSO_4.6H_2O$ and $MgSO_4.7H_2O$	6.37	...	...	40.74
L	$Na_2SO_4.10H_2O$, Na_2SO_4 and astracanite	7.71	18.67	15.50	...
M	Na_2SO_4, NaCl and astracanite	12.59	1.01	29.67	...
N	$MgSO_4.7H_2O$, $MgSO_4.6H_2O$ and astracanite	12.03	...	9.79	20.47
O	$MgSO_4.7H_2O$, $MgSO_4.6H_2O$ and NaCl	6.53	...	2.20	39.94
P	$MgSO_4.6H_2O$, NaCl, and $MgCl_2.6H_2O$	2.53	...	0.18	53.88

In Table I the concentrations are expressed in terms of the number of moles of salts whose formulas are given, per 1000 moles of water; in Table II the composition of these solutions is expressed in grams of these salts per 100 g. of water.

DISCUSSION OF RESULTS

(1) CRITICAL POINTS REPRESENTING THE COMPOSITION OF SOLUTIONS SATURATED WITH RESPECT TO A SINGLE SOLID

POINT A. SATURATION WITH RESPECT TO $MgSO_4.7H_2O$—The result obtained (54.36) is in fair agreement with that obtained by van Klooster[2] (54.7), but differs decidedly from the earlier result (58.0) of Lowenhertz,[1] which was used in the Hildebrand diagram.

POINT B. SATURATION WITH $Na_2SO_4.10H_2O$—This value, 35.4, was reported in the preceding paper of this series[2] and is in good agreement with the value 35.5 found by Seidell.[3]

POINT C. SATURATION WITH NaCl—This value, 54.9, is also taken from previous work of the writer and is in good agreement with the recent determinations.

POINT D. SATURATION WITH $MgCl_2.6H_2O$—This value, 103.9, represents the mean of three closely agreeing determinations. The value found by Lowenhertz[1] and used in the Hildebrand diagram was 108. A more recent value obtained by Biltz and Marcus[4] was 104.5.

(2) CRITICAL POINTS REPRESENTING THE COMPOSITION OF SOLUTIONS SATURATED WITH RESPECT TO TWO SOLIDS

POINTS E AND F—Some difficulty was experienced in determining the positions of these points owing to formation of solutions supersaturated with respect to astracanite, as is indicated by the fact that solutions corresponding to the point *r* on the curve AE and to the point *s* on the curve BF were prepared without difficulty; obviously astracanite can exist in equilibrium with solutions of the composition *r* and *s* as a *m*-stable form only. This salt invariably separated in the form of a dense crust composed of small crystals, which usually show only poorly defined planes. It was found possible to prepared small but well-formed crystals, one of which is represented in Fig. 2. This figure represents a sketch based upon such measurements as could be made by rotating the slide sustaining the crystal with respect to the cross hairs of a microscope. The values obtained for the composition of the Solutions E and F are comparable with those obtained by Roozeboom[5] at 24.5°, who found for E, 47.6 $MgSO_4$ and 26.85 Na_2SO_4 instead of 47.99 $MgSO_4$ and 24.97 Na_2SO_4; and for F, 36.25 $MgSO_4$ and 34.5 Na_2SO_4 instead of 37.96 $MgSO_4$ and 34.36 Na_2SO_4.

POINTS G AND H—The values of these points were determined and reported in the previous article of this series.[2] The corresponding values obtained by interpolation from the data reported by Seidell[6] are for G, 27.42 Na_2Cl_2 and 28.00 Na_2SO_4 instead of 29.0 Na_2Cl_2 and 27.5 Na_2SO_4; and for H, 49.30 Na_2Cl_2 and 11.41 Na_2SO_4 instead of 49.56 Na_2Cl_2 and 12.44 Na_2SO_4.

POINT I. SATURATION WITH $MgCl_2.6H_2O$ AND NaCl—It was not found possible to ascertain the correct position of this point or to show that there is a discontinuity in the curve connecting the points C and D. The solutions obtained by adding NaCl to solutions already saturated with $MgCl_2.6H_2O$ and stirring for a period of 5 days, showed on analysis only negligible amounts of sodium, and those obtained by adding increasing amounts of $MgCl_2.6H_2O$ to saturated solutions of NaCl also finally attained a composition corresponding essentially to that of solutions saturated with pure $MgCl_2.6H_2O$. This indicates that the point I approaches so nearly the position of the point D that it cannot be distinguished from the latter by the ordinary methods of analytical procedure. No evidence of the formation of solid solutions composed of $MgCl_2.6H_2O$ with small concentrations of NaCl could be obtained. It was also pointed out to the writer by Prof. G. N. Lewis that the line CD must approach the BD axis asymptotically since intersection with it would imply a negative value for the solubility of sodium chloride. This relation is of general application to similar cases but is of peculiar significance in dealing with a pair of salts which differ so greatly in solubility as those considered here and explain why difficulty was experienced in recognizing a discontinuity on the curve.

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[1] THIS JOURNAL, **10** (1918), 344.

[2] *J. Phys. Chem.*, **21** (1917), 513.

[1] *Z. physik. Chem.*, **13** (1894), 478.

[2] *Loc. cit.*

[3] *Am. Chem. J.*, **27** (1902), 52.

[4] *Z. anorg. Chem.*, **71** (1911), 168.

[5] *Z. physik. Chem.*, **2** (1888), 518.

[6] *Am. Chem. J.*, **27** (1902), 56.

The work of van't Hoff and Meyerhoffer[1] assigns to the point under discussion a definite position corresponding to a solution represented by the composition 103 $MgCl_2$ and 2.50 Na_2Cl_2.

The points on the curve CI are of much interest in showing that the rate at which the solubility of NaCl is decreased by increasing concentrations of $MgCl_2$ is far from uniform. This and similar curves on this diagram also show how large an error is involved in the assumption commonly made in preparing such diagrams where the critical points are connected by straight lines.

POINTS J AND K—These points represent the composition of solutions saturated with respect to $MgCl_2.6H_2O$ and $MgSO_4.6H_2O$, and with respect to $MgCl_2.6H_2O$ and $MgSO_4.7H_2O$, respectively. The heptahydrate of magnesium sulfate rapidly changed into the hexahydrate when stirred with solutions whose composition varied from J to K. The crystals thus obtained showed monoclinic symmetry, but owing to the number and variations in the relative development of the faces represented, the range of crystal habit exhibited by them was large. One example of a well-developed crystal is shown in Fig. 2. A value of approximately 86° for the angle α shown in this sketch is characteristic of this hydrate. When brought into contact with a drop of water on the stage of the microscope, these crystals rapidly changed into a mass of *o*-rhombic prisms with abrupt terminations which are easily identified as crystals of the heptahydrate.

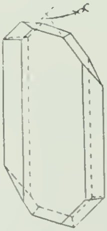

FIG. 2—$MgSO_4.6H_2O$

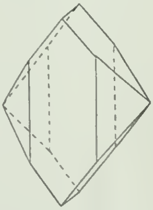

FIG. 3—ASTRACANITE

No definite evidence for the formation of any other hydrates along the line JK could be obtained, and the crystals showing the wide range of variation in habit already referred to were shown to be stable in the same solution even when the composition of this solution varied with respect to the concentrations of magnesium chloride present. Van't Hoff and Estreicher[1] were able to prepare hydrates of magnesium sulfate containing five and four molecules of water, and also to ascertain the composition of solutions saturated with respect to the hexa- and penta- and the penta- and tetrahydrates, which solutions correspond to points on the line JK. Subsequently van't Hoff and Estreicher[1] concluded that the penta- and tetrahydrates were *m*-stable at all temperatures, as a result of a study of the dissociation pressures of these hydrates, and it is not improbable that neither of the lower hydrates was actually present as solid phases in contact with the saturated solutions prepared and analyzed by them.

The values found for the points J and K differ greatly from those obtained by Lowenhertz[2] who reported for J, 104 $MgCl_2$ and 14 $MgSO_4$ instead of 102.1 $MgCl_2$ and 5.40 $MgSO_4$; and for K, 73 $MgCl_2$ and 15 $MgSO_4$ instead of 77 $MgCl_2$ and 9.53 $MgSO_4$. His values appear on the diagram at the points J′ and K′. The large discrepancy between the two sets of values can be attributed to the indirect method used by Lowenhertz for the determination of sulfate ion, namely, addition of a known amount of lead nitrate, separation of the lead sulfate, precipitation of lead in the filtrate as lead sulfide removal of the lead sulfide and determination of the nitric acid in the filtrate by titration with sodium hydroxide solution. This method clearly offers more and larger sources of error than the direct separation of sulfate ion as barium sulfate used by the writer.

(3) CRITICAL POINTS REPRESENTING THE COMPOSITION OF SOLUTIONS SATURATED WITH RESPECT TO THREE SOLIDS

POINT L. SATURATION WITH RESPECT TO Na_2SO_4, $Na_2SO_4.10H_2O$ AND ASTRACANITE—This is one of the points for which no data were previously available. The values found are in fair agreement with the position assumed in the Hildebrand diagram.

POINT M. SATURATION WITH RESPECT TO NaCl, Na_2SO_4 AND ASTRACANITE—This point was fixed by the work of van't Hoff and Meyerhoffer[3] who found as the mean of four experiments 46 Na_2Cl_2, 16.5 $MgSO_4$ and 3 Na_2SO_4 instead of 45.72 Na_2Cl_2, 18.84 $MgSO_4$ and 1.28 Na_2SO_4, representing the mean of five closely agreeing results obtained by the writer.

POINT N. SATURATION WITH RESPECT TO ASTRACANITE, NaCl, AND $MgSO_4.7H_2O$—This point was also fixed by the work of van't Hoff and Meyerhoffer[4] who found as the mean of two experiments 26 Na_2Cl_2, 34 $MgSO_4$, 7 $MgCl_2$, corresponding to the point N′ on the diagram (Fig. 1) instead of 15.08 Na_2Cl_2, 18 $MgSO_4$, and 38.71 $MgCl_2$ found by the writer. The correctness of the latter values seems to be sufficiently confirmed by the positions found for a number of points on the lines EN, MN, and ON.

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[1] *Sitzb. Akad.*, Berlin, 1898, 591.

[1] *Sitzb. Akad.*, Berlin, 1898, 488, 497.

[2] *Loc. cit.*

[3] *Sitzb. Akad.*, Berlin, 1898, 594.

[4] *Loc. cit.*

POINT O. SATURATION WITH RESPECT TO $MgSO_4.7H_2O$, $MgSO_4.6H_2O$, AND NaCl—The values obtained by van't Hoff and Meyerhoffer[1] for this point were 10.5 Na_2Cl_2, 53 $MgCl_2$, and 15 $MgSO_4$ which are represented by the point X′ on the line ON of the diagram.

POINT P. SATURATION WITH RESPECT TO $MgSO_4.6H_2O$, $MgCl_2.6H_2O$ AND NaCl—The values obtained by van't Hoff and Meyerhoffer,[1] namely, 1 Na_2Cl_2, 102 $MgCl_2$, and 5 $MgSO_4$, are in fair agreement with those of the writer, namely, 0.28 Na_2Cl_2, 101.85 $MgCl_2$, and 3.78 $MgSO_4$.

(4) ELIMINATION OF KIESERITE FROM THE SYSTEM

The work of van't Hoff seems to show that $MgSO_4.H_2O$, kieserite, should be formed in this system at 25° from solutions whose composition is represented by a very small field below and to the left of the point P, but not in solutions represented by the point J, that is, solutions saturated with $MgCl_2.6H_2O$ and $MgSO_4.6H_2O$ only. It does not seem probable that the vapor pressure of the solution of the composition P should be markedly less than that of the solution of the composition J, and it is therefore difficult to understand why the former should be able to change $MgSO_4.6H_2O$ into $MgSO_4.H_2O$ if the latter is unable to do so. Repeated attempts to prepare kieserite in such solutions, even when inoculated with small amounts of the pure hydrate, failed, and the writer is compelled to believe that it does not constitute a part of this system at a temperature of 25°.

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[1] *Loc. cit.*

LABORATORY AND PLANT

NEW TURBIDIMETER FOR SOLUTIONS OF GELATIN, CELLULOSE, AND VARNISHES

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Received August 12, 1919

Turbidimeters as used in water analysis, based on the vanishing of a line or filament for a given depth of liquid, are well known, the turbidities being expressed generally on an arbitrary scale. For this method there is generally assumed a more or less unlimited amount of the liquid.

In many cases, however, especially in research and development work with nonaqueous systems only a limited amount of the material may be available, for example, in development of a new lacquer or varnish. For such work an instrument operating on a small constant thickness becomes desirable. While this could be attained photometrically, measuring either the relative transmitted light (transparency) or the relative side scattered light (turbidity),[1] yet in some respects the method of judging distinctness of some standard object seems the simplest for practical purposes. What is required now for the case of a limited thickness of fluid is an object the visibility of which can be varied in some continuous and easily measurable way. For this purpose advantage was taken of the well-known properties of crossed gratings, on lines similar to those employed by H. E. Ives[2] in his test object for visual acuity. The essential part of the apparatus consists of two superposed opaque line gratings arranged to rotate relatively to each other about an axis perpendicular to their plane. Viewed by transmitted light, at such a distance that the grating lines are below the limit of resolution, parallel dark bands are seen. The separation of these alters quite continuously as the gratings are rotated, so that we have a continuous change from extreme visibility to invisibility—when the bands can no longer be resolved. The average brightness of the field remains constant, and also the variation of brightness from the center of a bright band to that of the adjacent dark band is the same for all sizes of bands.

The following diagrams, taken from H. E. Ives' paper, illustrate the important relationship between the width of the irradiation bands and the angle of relative rotation of the gratings.

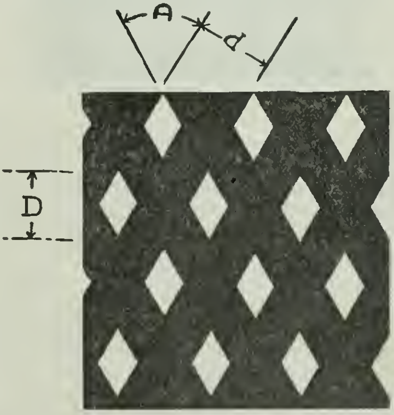

Fig. 1

In Fig. 1, d is the distance between centers of the grating lines, A the angle of relative rotation, and D the distance between those regions where continuous straight lines can be drawn across without meeting a clear space. These latter lines form the centers of the dark bands visible on viewing the crossed gratings.

The distance between them is given by the formula

$$D = \frac{d}{2 \sin A/2}.$$

In Fig. 2 is shown a photomicrograph of a pair of crossed gratings, turned through a small angle. At a sufficient distance—several yards—the component lines vanish, only the interference (or irradiation) bands showing. At the ultimate resolving distance the variation of intensity over the width of the bands is lost and they appear as sharp, black lines. For details as to their use in forming visual acuity tests, reference should be made to Ives' paper. Their application to turbidimetry depends on an inversion of the same principles. If a scattering (turbid) medium be placed in front of the crossed gratings, the visibility limit $1/D = 2 \sin A/2$ will be lowered, according to the turbidity. For relatively small angles, secured by a proper choice of *d*, the expression $1/D = 2 \sin A/2$ reduces to $1/D = \sin A = A$; from this the visibility limit—for one and the same observer, *i. e.*, for the same visual acuity—can be measured by the angle through which the gratings must be turned to make the bands just disappear.

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[1] A convenient apparatus for this will be described in a later paper.

[2] *Elec. World*, **1910**, p. 939; *J. Opt. Soc. Am.*, **1917**, p. 100.

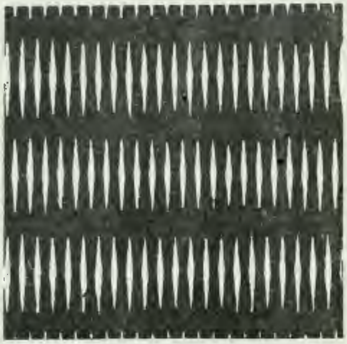


FIG. 2

If now, $A_{max.}$ be the angle for the visibility limit for a given thickness of some standard medium, *e. g.*, distilled water, lacquer solvent, and A the angle for the same thickness of a turbid solution, then putting $A_{max.}/A = 100/C$, gives C, the per cent clarity, from $C = \frac{100\ A}{A_{max.}}$.

The instrument constructed for measuring clarities in this way is shown in Fig. 3. The solutions to be tested are conveniently put up in 8-oz. square jars, with screw-on caps. These are obtainable commercially and are much more convenient for work with varnishes, lacquers and other sticky substances than corked or stoppered bottles. Since, however, the sides are not perfectly plane parallel, distortions of the grating image will occur on placing in position in front of the gratings. To eliminate this refraction error, the test jars are placed in a cell with glass walls parallel to the gratings, and immersed in a liquid of refractive index equal to the glass, monochloronaphthalene proving very satisfactory and eliminating all distortion. The readings of A are made on a circle and vernier reflected in the concave mirror above, readings being possible to 2′ of arc. Error in zero can, if necessary, be eliminated by alternate reading on either side. Readings can be taken so rapidly that it is easy to secure a mean of 5 or 6 for each observation. As with all methods depending upon visibility of interference fringes, the possible precision is much higher than that practically obtainable, owing to the fatigue factor in making such readings. But this error, for a normal observer, does not appear to be at all prohibitive, as the following results indicate. They were made without special precautions, such as dark room, resting the eye, or head rest, and the gratings were not of first-class quality.

SAMPLE	A	P. E.	C	P. E.
Solvent	41°24′	±16′	100	....
Dope 1	2°30′	± 2′	6.0	±0.2
Dope 2	3°38′	± 9′	8.7	±0.4
Dope 3	10°15′	±17′	24.7	±0.5
Dope 4	22° 0′	± 8′	53.1	±0.5
Dope 5	30°28′	±21′	73.5	±0.95
Dope 6	35°10′	±23′	84.9	±1.00

The probable error for A is for the mean of five readings, hence the P. E. for a single observation would be larger, amounting for the largest value to 10 per cent on the reading. The P. E. on the per cent clarity C is calculated from the value

$$\text{P. E.} = \pm \frac{\sqrt{\left(\frac{Aa}{A_{max.}}\right)^2 + b^2}}{A_{max.}} \times 100$$

where $A_{max.}$ = reading for solvent; A = reading for sample; *b* = P. E. for setting of A; *a* = P. E. for setting of $A_{max.}$.

The probable error of a single setting increases on the whole with the angle of setting, *i. e.*, with the clarity, but the per cent P. E. remains much the same. The readings are made as rapidly as with the polarimeter or refractometer.

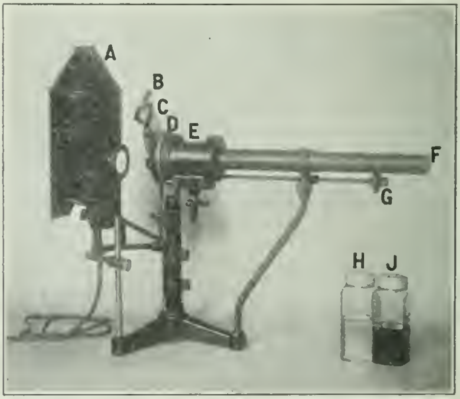


FIG. 3

A—Concentrated filament lamp and hood
B—Mirror for reading scale
C—Diffusing and reducing glasses
D—Grating mounts, with vernier and scale
E—Cell to hold sample
F—Eyepiece
H—Sample clear liquid
J—Sample lacquer

In the instrument constructed two photographic line gratings were used, having about 50 lines per in., and $A_{max.}$ was about 40° for normal visual acuity. The error using the simplified formula

$C = A/A_{max.} \times 100$ instead of $\frac{\sin A/2}{\sin A_{max.}/2} \times 100$ is not, however, serious for the work required. Thus for $A = 5°$, $A_{max.} = 40°$, we have

	Approximate	Accurate
C =	12.5 per cent	12.7 per cent

There appear to be several advantages in replacing such expressions as "water-clear," by definite per cent clarity and definite colorimetric values, where color is a factor.

Figs. 1 and 2 are reproduced by kind permission of Mr. H. E. Ives and the American Optical Society from the *Journal of the Optical Society of America*. My thanks are also due to Mr. Tompkins for assistance in making observations and computations.

THE EFFECT OF CHLORIDES ON THE NITROMETER DETERMINATION OF NITRATES[1]

By M. T. Sanders

Forcite Experimental Laboratory, Atlas Powder Co., Landing, N. J.

The nitrometer furnishes a very rapid and accurate means of analyzing a substance which quantitatively liberates a gas when treated with liquid reagents, and is usually used to determine nitrogen in nitrates. The nitrate solution is washed into the decomposing bulb and some sulfuric acid drawn in after it. In the presence of the acid, the mercury reduces the nitrate, liberating nitric oxide. The gas is then run into the measuring tube, allowed to cool, and the volume read. Nitrometer measuring tubes are of two kinds, one for guncotton, which is graduated to read per cent nitrogen when a one-gram sample is used; the other, the so-called "universal tube," is so graduated that 0.01 mole of a gas, at 20° C. and 760 mm., will read 100.

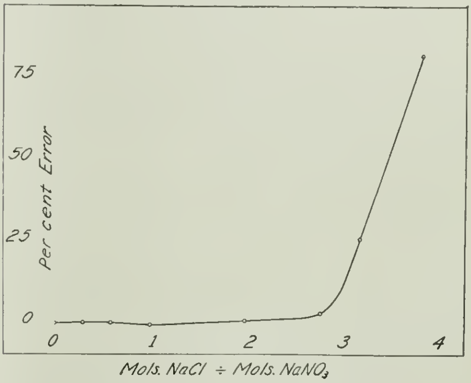
Crude sodium nitrate nearly always contains a few per cent sodium chloride. The purpose of this work was to determine the maximum quantity of sodium chloride which can be present in the sample and yet permit accurate analyses to be made on the nitrometer. As no reference to the effect of sodium chloride on the nitrometer determination of nitrates could be found in such literature as was available at the laboratory, it was thought best to determine the accuracy of the nitrometer method for samples of sodium nitrate containing varying quantities of sodium chloride.

The samples used in the nitrometer are small, 0.85 g. for sodium nitrate. To avoid the difficulty involved in mixing small quantities of the dry salts, nearly saturated solutions of sodium nitrate and sodium chloride were made up, and the samples prepared by mixing weighed portions of these solutions in a bottle.

The actual sample for analysis was weighed by means of a Lunge pipette. The procedure was as follows: The three-way stopcock and capillary tube of the decomposing bulb were filled with mercury. The sample was placed in the cup of the decomposing bulb and drawn into the bulb. The cup was then washed with 2 one cc. portions of water, followed by 25 cc. of 96 per cent sulfuric acid in three or four portions.

The decomposition was started by gentle shaking of the bulb. When the gas was no longer rapidly liberated, the decomposing bulb was put under a vacuum of 10 in. of mercury, the lower stopcock closed, and the bulb shaken violently for 4 min. The liberated gas was run into the measuring tube, allowed to cool for 15 min., and the reading taken.

A mirror was used in comparing the levels of mercury in the various tubes, thus avoiding any errors due to parallax. The samples used were of such size that the effect of slight errors in reading the volume of gas would be negligible.



The more chlorides in the sample, the more sludge was formed in the decomposing bulb, and the more difficult it was to clean the mercury in the decomposing bulb preparatory to the succeeding determination. It will be noticed in Table I that duplicate determinations on samples high in chlorides did not check well. This is probably due to the fact that the sludge in the decomposing bulb trapped some of the gas.

Table I

$\frac{\text{Moles NaCl}}{\text{Moles NaNO}_3}$	Per cent $NaNO_3$ by Analysis I	II	Mean of Results Per cent $NaNO_3$	Per cent $NaNO_3$ Actually Present	Error	Per cent Error
0.00	42.21	42.20	42.21	42.18	+0.03	+0.07
0.2918	31.87	31.90	31.89	31.86	+0.03	+0.09
0.5749	25.63	25.64	25.64	25.58	+0.06	+0.23
0.9776	20.22	22.13	22.18	20.24	—0.06	—0.30
1.950	13.57	13.31	13.44	13.34	+0.10	+0.75
2.728	11.00	10.63	10.82	10.48	+0.34	+0.324
3.129	11.82	11.99	11.90	9.44	+2.46	+26.1
3.782	14.96	14.68	14.82	8.12	+6.70	+62.5

From the compositions and weights of the solutions of sodium nitrate and sodium chloride used, the per cent of sodium nitrate actually present in the sample was calculated. The results of the nitrometer determinations were also calculated as sodium nitrate. From these figures the percentage error of each determination was calculated.

In Table I are tabulated the ratio of moles of sodium chloride to moles of sodium nitrate in the sample used, the actual per cent of sodium nitrate present, the per cent of sodium nitrate as determined on the nitrometer, and the percentage error of each determination. This table shows that if the percentage error in a determination is to be kept below the usual value of 0.1, the ratio of the moles of sodium chloride to moles of sodium nitrate present in the sample must be less than 1 : 3. This corresponds to about 17 per cent sodium chloride in a mixture of the dry salts.

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 5, 1919.

When the ratio of the moles of sodium chloride to moles of sodium nitrate and the percentage error are plotted, it is seen that the curve makes a sharp break at the point where

$$\frac{\text{Moles NaCl}}{\text{Moles NaNO}_3} = 3.0.$$

This is also the ratio of $\frac{\text{Moles HCl}}{\text{Moles HNO}_3}$ in the equation

$$3HCl + HNO_3 = NOCl + Cl_2 + 2H_2O.$$

It is probable that this reaction takes place in the decomposing bulb. The nitrosyl chloride attacks the mercury and liberates nitric oxide, which, recombining with the free chlorine, repeats the cycle until all the free chlorine is used up.

If an excess of sodium chloride were present, hydrochloric acid would be formed, and the gas in the measuring tube would be a mixture of hydrochloric acid and nitric oxide. Tests showed that under these conditions hydrochloric acid and nitric oxide were actually present. No attempt was made to prove the absence of chlorine in these gases, or to show that the sludge in the decomposing bulb contained chlorides of mercury.

In conclusion it may be stated that it was impossible to obtain results accurate to 0.1 per cent if the sample contained more than 15 to 17 per cent sodium chloride, on a dry basis.

A MODIFICATION OF THE THOMPSON METHOD FOR THE DETERMINATION OF ACETIC ACID IN WHITE LEAD

By L. McMaster and A. E. Goldstein

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Received August 18, 1919

Of the several methods described in the literature for determining acetic acid in white lead, that of Thompson[1] is the most reliable, both for white leads which have not been ground in oil and for those from which the oil has been extracted.

In this method 18 g. of dry white lead are placed in a 500 cc. flask which is arranged for connection with a steam supply and also with a condenser. To the white lead are added 40 cc. of sirupy phosphoric acid, 18 g. of zinc dust, and about 50 cc. of water. The mixture is distilled down to a small bulk and steam passed in until the flask is half full of water, when the steam is shut off and the mixture again distilled to the same bulk. This operation is conducted twice. The distillate is then transferred to a special flask and one cc. of sirupy phosphoric acid added. This mixture is distilled until about 20 cc. remains in the flask, and steam is passed through the flask until it contains about 200 cc. of condensed water, when the steam is shut off and the liquid again distilled. These operations are repeated until 10 cc. of the distillate require but one drop of $N/10$ alkali to change the color of phenolphthalein. The bulk of the distillate is titrated with $N/10$ alkali, and the acetic acid calculated.

We have used this method to determine the acetic acid in a number of samples of white lead, but the method is long and tedious, and it is necessary to use a special, rather fragile flask. Thompson states that "if the dry white lead under examination has been obtained by the extraction as a residue from white lead paste, it is well that this extraction should be exceedingly thorough, as otherwise fatty acids may be held and distilled with the acetic acid. Even then they will not interfere with the final titration, as they may be filtered from the distillate before titration." In the analysis of a number of samples of extracted white lead by this method we were never able to get a clear filtrate free from fatty acids, even after long extraction; nor were we able to remove all of the fatty acids by filtration since a great part of them was present in colloidal suspension. The results, therefore, were always somewhat high.

We have found that the time of an analysis can be materially shortened, and the passing over of the fatty acids into the distillate obviated by performing one initial steam distillation followed by a second distillation under reduced pressure.

The reduced-pressure method is as follows: 18 g. of extracted white lead are placed in an ordinary 500 cc. flask, arranged for connection with a steam supply and also with a condenser, and 40 cc. of sirupy phosphoric acid (85 per cent) and 50 cc. of water are added. The flask is heated directly and the material distilled down to a small bulk. Steam is next passed into the flask and the distillation continued until about a 600 cc. distillate is obtained. After adding about 0.5 cc. of the phosphoric acid, the distillate is transferred to a heavy-walled flask. Into the neck of the flask is inserted a two-hole stopper. Through one hole is passed a very small bore capillary tube through which a minute stream of air is allowed to pass during the distillation. Through the other hole is passed a connecting bulb tube attached to a condenser. The whole apparatus is so arranged that the distillation may be conducted under a reduced pressure of about 150 mm., using an Erlenmeyer filtering flask as a receiver. When 10 cc. of the distillate require but one drop of $N/10$ alkali to produce a color change in phenolphthalein, the distillation is stopped, the distillate titrated with $N/10$ alkali and the acetic acid calculated. It is seldom necessary to distil over more than 500 cc. At no time should the liquid in the distilling flask be allowed to go much below 100 cc. because of the fact that phosphoric acid is often drawn over by the suction.

We have used the same quantities of materials as were used by Thompson so that the two methods could be compared. We found it unnecessary to use the zinc dust.

A series of determinations was carried out by the Thompson method and by the reduced-pressure method on a sample of white lead, made by the old Dutch process, which had been ground in oil. As much as possible of the linseed oil was first removed by shaking the white lead with portions of gasoline until the supernatant liquid was no longer yellow on standing with the white lead for several hours. The greater part of the gasoline was decanted and the remainder removed by filtration with suction. The white lead was then dried and extracted with ether for 72 hrs. by the Soxhlet method.

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[1] *J. Soc. Chem. Ind.*, **24** (1905), 487.

Expt.	Per cent Acetic Acid Thompson Method	Per cent Acetic Acid Reduced-Pressure Method
1	0.035	0.031
2	0.035	0.031
3	0.035	0.032
4	0.036	0.031
5	0.035	0.032
6	0.036	0.032
7	0.035	0.031
8	0.035	0.031

Although the results by the Thompson method check with each other, every distillate was cloudy from fatty acids in spite of the very thorough extraction; furthermore, we were not able to remove all of the fatty acids by filtration. By the other method, regardless of how cloudy the initial distillate may have been, the final distillate was always perfectly clear and the results obtained are accordingly slightly lower than those obtained by the Thompson method. If the sample had not been so thoroughly extracted, there would have been greater differences between the results obtained by the two methods, and in a commercial analysis of white lead such a long extraction is seldom made.

We have also used the reduced-pressure method for several determinations of acetic acid in white lead, ground in oil, without first extracting the oil, and find that we can obtain results that agree not only with each other but also with those obtained on the extracted sample. It is, of course, necessary to know the per cent of oil in the sample. Further experiments will be made on this part of the work.

It is thus seen that more accurate results can be obtained by this reduced-pressure method than by the Thompson method. The time necessary for a determination is also shortened and the use of a fragile special flask is unnecessary.

A RAPID METHOD FOR THE DETERMINATION OF SULFUR IN PETROLEUM OILS

By A. W. Christie and C. S. Bisson

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Received August 13, 1919

In the examination of petroleum oils, two of the most important determinations are fuel value and sulfur content. The rinsings from the bomb after a determination of the fuel value not only serve as a means of finding the total acidity due to nitric and sulfuric acids, but also furnish a solution which can be used for the determination of sulfur. As shown by previous investigators,[1,2] the combustion of fuels in the calorimetric bomb under an oxygen pressure of 30 atmospheres insures complete oxidation of sulfur to sulfur trioxide. The resulting sulfuric acid is usually determined gravimetrically as barium sulfate.

For an accurate determination of sulfur, the barium sulfate must be allowed to stand several hours before filtration. This, together with the time necessary to filter, wash, dry, ignite, cool, and weigh the precipitate, makes the determination very long. Furthermore, in the analysis of oils containing very small amounts of sulfur the weight of barium sulfate obtained is so small as to make results inaccurate. A method which would be accurate for small amounts of sulfur and which could be completed in a short time would have distinct advantages over the barium sulfate determination. Such a method was proposed by Raiziss and Dubin.[1] The procedure consists in the separation of the sulfur as insoluble benzidine sulfate and the subsequent titration of the benzidine in acid solution with potassium permanganate.

METHOD

After the combustion of a 0.5 to 0.6 g. sample of oil in a calorimetric bomb, the contents of the bomb are washed through filter paper into a 250 cc. beaker. The total acidity of this solution is then determined by titration with standard alkali. The solution is made to such a volume in a calibrated flask that a 25 cc. aliquot part will contain between 0.2 and 1.5 mg. sulfur. (The total acidity will give an indication of the amount of sulfur present.) A 25 cc. aliquot part is placed in a 300 cc. wide-mouthed conical flask and acidified with one drop of dilute hydrochloric acid. Ten cc. of a benzidine hydrochloride solution (8 g. per l.) are added, the solution shaken several times, and allowed to stand 15 min. or longer. It is then filtered on a small asbestos pad supported by a Witt filter plate in a Gooch filter tube. (The asbestos should have been previously treated with potassium permanganate.) The flask is washed 3 times with approximately 5 cc. cold water, allowing each portion to run through before the succeeding portion is poured on the filter. The asbestos pad and precipitate are then washed back into the original flask with distilled water. One cc. of 10 per cent sodium hydroxide is added and the solution allowed to heat on the steam bath a few minutes to dissolve the benzidine sulfate. Water is then added to bring the volume to about 100 cc. and 5 cc. concentrated sulfuric acid added. The flask is returned to the steam bath and when hot the solution is titrated with $N/20$ potassium permanganate until the yellow color which first forms has disappeared and the red color slowly fades. An excess of 10 cc. of permanganate is added and the flask replaced on the steam bath for exactly 10 min. Ten cc. of approximately $N/20$ oxalic acid are added and as soon as the solution clears the titration with $N/20$ potassium permanganate is continued to a permanent pink color. The total number of cubic centimeters of $N/20$ potassium permanganate used minus the volume of $N/20$ potassium permanganate equivalent to the oxalic acid used, multiplied by the factor

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[1] S. H. Regester, This Journal, **6** (1914), 812.

[2] A. C. Fieldner, Bureau of Mines, *Tech. Paper* **26**, 10.

[1] *J. Biol. Chem.*, [2] **18**, 297.

0.041 gives the number of milligrams sulfur in the aliquot part from which the percentage of sulfur can be calculated. The factor 0.041 has been established by the analyses of solutions of known sulfate content.

The above method has been used to determine the sulfur content of several fuel oils and the results of duplicate determinations on different weights of oil are tabulated in Table I, together with the percentage of sulfur obtained by the gravimetric barium sulfate method.

TABLE I—PERCENTAGES OF SULFUR IN FUEL OILS

SAMPLE No.	BARIUM SULFATE METHOD Per cent	BENZIDINE SULFATE METHOD Per cent
1	0.71	0.73
	0.74	0.71
2	0.96	0.97
	0.96	0.97
3	0.97	0.92
	0.87	0.96
4	0.83	0.85
	0.77	0.85
5	1.70	1.71
	1.66	1.72

From a consideration of Table I it is evident that the volumetric method gives essentially the same result as the gravimetric method, and, on the whole, closer agreement between duplicates is obtained by the benzidine method. In each of the benzidine sulfate determinations, the aliquot parts used never exceeded one-fourth of the bomb rinsings. By using the entire rinsings, after concentration to 25 cc. or less, equally accurate results could be obtained on oils containing only 0.1 per cent sulfur. After the titration of the bomb rinsings, the time required to complete a sulfur determination by the volumetric method is about 45 min., as compared with several hours for the barium sulfate method.

SUMMARY

I—A rapid volumetric method for the determination of sulfur in petroleum oils is described.

II—After combustion of the oil in a bomb, the sulfur is separated as insoluble benzidine sulfate and determined by titration with standard potassium permanganate.

III—Comparative analyses show that this method gives as accurate results as the barium sulfate method.

THE FORMALDEHYDE METHOD FOR DETERMINING AMMONIUM NITRATE[1]

By J. T. Grissom

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In the manufacture of ammonium nitrate by the double decomposition method it is necessary to keep a close analytical control of the percentage of ammonium nitrate in the reacting system. A study was made of the various proposed methods of determining ammonium salts with a view of selecting a rapid method which would give sufficiently accurate results for chemical control.

There are three more or less standard methods in general use for analyzing ammonium nitrate, *i. e.*, the Kjeldahl method, the nitrometer method, and the impurity method. The first two are very accurate, but take from 3/4 to 1 1/2 hrs. for duplicate analyses, which is too long for most control work. The third method, while commonly used, is unsatisfactory, in that any errors of omission or commission are combined here.

A fourth method, making use of formaldehyde, is much more rapid but likely to give results from 0.5 to 1, or even more, per cent low. The method depends upon the ease with which formaldehyde reacts with ammonia or ammonium salts to form hexamethylenetetramine:

$$6CH_2O + 4NH_4NO_3 + 4NaOH = C_6H_{12}N_4 + 4NaNO_3 + 10H_2O$$

The method is very simple and in general is as follows: A neutral[1] 20 per cent solution of formaldehyde is added to the ammonium nitrate solution, warmed, and titrated with standard NaOH, using phenolphthalein as indicator, since the latter is not sensitive to hexamethylenetetramine. The amount of NaOH used gives the amount of ammonium nitrate present. There are certain objections to this method. In titrating at room temperature the reaction is slow, but by heating to 60° C. before titrating, the same end-point is obtained in a much shorter time. Upon heating to higher temperatures before titrating, however, low results are obtained. This is probably due to the conversion of hexamethylenetetramine back to ammonia at high temperatures.

The formaldehyde method was compared with the other three with a view of finding out why the results were low and of modifying it so as to obtain accurate and rapid results.

A sample of pure ammonium nitrate was prepared by repeated recrystallization until no tests were given for chlorides, sulfates, nonvolatile residue and insoluble residue. The results of check analyses are shown in the table.

ANALYSIS OF PURIFIED AMMONIUM NITRATE—PER CENT NH_4NO_3

				FORMALDEHYDE METHOD					
				Direct Titration NaOH				Excess NaOH	
	KJELDAHL	NITROMETER	IMPURITY	2*N*	*N*	*N*/3	*N*/10	*N*/3	*N*/10
	99.84	99.85	99.845[1]	99.15	99.20	99.59	98.79	100.10	99.01
	99.79	99.78	.....	99.07	99.32	99.50	98.93	100.15	98.87
	99.82	99.88	.....	....	99.28	99.56	98.89	100.14	....
	...	99.88	.....	....	....	....	....	....	....
Av.	99.82	99.85	99.845	99.11	99.27	99.55	98.87	100.13	98.94
DIFF.[2]	0.0	+0.30	+0.025	—0.71	—0.55	—0.27	—0.95	+0.31	—0.88

[1] NH_4NO_3 determined by difference—Triplicate of very closely checking analyses gave moisture 0.14 per cent; acidity (HNO_3) 0.015 per cent; sulfates, chlorides, insoluble and nonvolatile, none.

[2] Kjeldahl taken as standard.

It will be noted that the above formaldehyde determinations were made in part by direct titration and in part by using an excess of standard sodium hydroxide solution and titrating back with standard acid.[2] Direct titration with *N*/3 NaOH gives the best results. In the presence of an excess of alkali, some of the formaldehyde is apparently converted into formic acid, *i. e.*, sodium formate. For example, 32.78 cc. normal NaOH were added to 25 cc. neutral 20 per cent formaldehyde solution. After warming to 60° C., the solution was titrated with normal H_2SO_4 and required only 31.00 cc., showing that an acidity of 1.78 cc. $N/1$ H_2SO_4 had developed. The more dilute the alkali, the less marked is this reaction.

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[1] Read before the Division of Industrial and Engineering Chemistry at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 5, 1919.

[1] Exactly neutralized with *N*/3 NaOH, using phenolphthalein as indicator.

[2] G. H. C. van Bers, *Chem. Weekblad*, **14** (1917), 968–75; *J. Chem. Soc.*, **112**, II, 578; *Chem. Abs.*, **12** (1918), 1447.

CONCLUSIONS

The rapid formaldehyde method for ammonium nitrate invariably gives low results by direct titration. By using an excess of alkali and titrating back, less reliable results are obtained, presumably owing to the formation of formic acid.

Direct titration with a $N/3$ NaOH solution gives results which are consistently about 0.25 per cent low. It would seem, therefore, that this method may be used for accurate work if a suitable correction is made by adding a constant factor to the results. This factor is obtained by running a Kjeldahl on a representative sample and comparing the result with that obtained by the formaldehyde method, using $N/3$ NaOH.

THE PREPARATION OF HEMATOXYLIN

By Percy A. Houseman and Clement K. Swift

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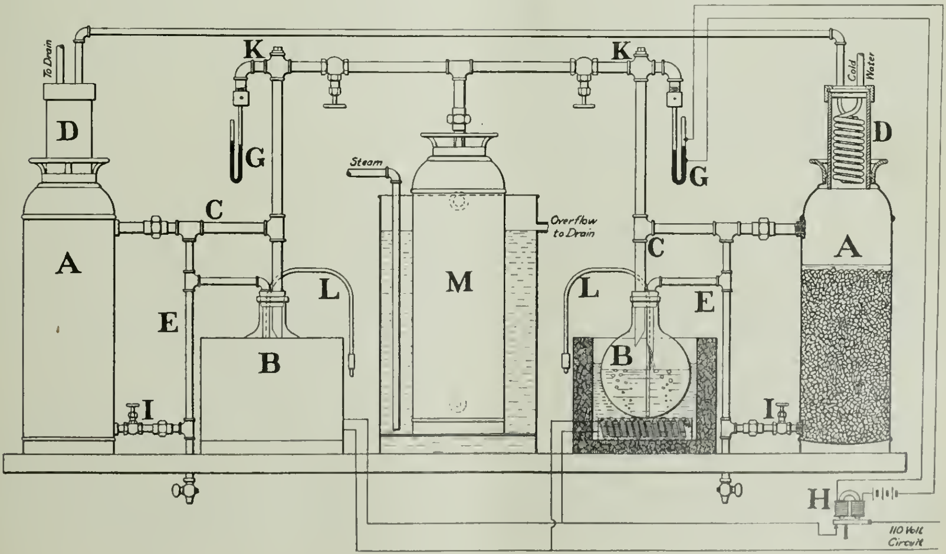
Received August 7, 1919

Hematoxylin has hitherto been made almost exclusively in Germany. During the war, a relatively large amount of hematoxylin was required for use in surgery as a bacterial stain, and in this emergency practically none was obtainable. A method was therefore sought to manufacture pure hematoxylin in commercial quantity for supply to the American government.

The apparatus developed for this purpose is shown in the cut.

The raw material used is a powdered extract of logwood which is prepared from a mild aqueous extract of unoxidized logwood chips. The powdered extract is made into small briquettes which are broken into pieces and the dust screened out. The pieces are then filled into the extractors A. B are flasks containing ether, surrounded by oil which is directly heated by electrical heaters made of Monel metal wire wound on slate. The ether vapor passing up the pipes C enters the top of the extractors A, is condensed by the copper coils D, and drops back on the logwood extract, dissolving hematoxylin from it, and enters the flasks B again through the constant level syphons E. G are mercury manometers from which an electrical connection is made to relay H, which cuts off the current from the heaters if pressure develops in the apparatus through failure to condense all the ether. The apparatus runs day and night. Every fourth day the valves I are closed and all of the ether distilled from the flasks into the extractors A. About 1500 to 2000 cc. of cold water are then introduced at K to each of the flasks. The water is heated by the oil baths and dissolves the crude hematoxylin in the flasks. The solution is blown out through the tubes L, and filtered hot. After standing for several hours pure hematoxylin crystallizes from this solution in colorless needles which are filtered at the pump, washed with ice water and dried on a porcelain tray. The extractors are changed every ten days, the exhausted extractor being transferred to the position M and the ether recovered from a hot water bath.

The apparatus described produces 100 g. of pure hematoxylin per day, the comparatively low capacity being caused by the slight solubility of the hematoxylin in ether which, however, seems to be the only practicable solvent. The loss of ether is almost nil.



The apparatus functions practically as a large-scale Soxhlet extractor with constant instead of intermittent syphon. For extractors it has been found very convenient to use 3-gal. copper fire extinguishers.

The apparatus described in this article has been found very useful for other continuous extractions with organic solvents when it is desired to treat several kilograms of material.

METHOD OF PREPARING PHLOROGLUCINOL REAGENT FOR THE KREIS TEST

By **Henry W. Dixon**

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Received August 26, 1919

The Kreis[1] test has been found to be a useful chemical test for the detection and estimation of rancidity in fats when considered together with the taste, odor, and flavor. If a supply of phloroglucinol is not available, the Kreis reagent may be conveniently prepared by the following method, based on Barth and Schreder's synthesis of phloroglucinol from resorcinol.[2]

Dissolve 100 g. of sodium hydroxide in 40 cc. of water by heating slowly in an iron or nickel container. Cool to a temperature at which a few crystals of resorcinol dropped into the liquid do not become brown, and stir in 15 g. of resorcinol. Cover with a watch glass to exclude air and at the same time to permit observation, and heat for 2 or 3 hrs. in a sand bath until the melt is a dark chocolate-brown. (If the melt is heated too fast or too long, charring will take place with low yield of phloroglucinol. If the reaction is not carried to completion, unchanged resorcinol will interfere with the color of the Kreis test.) Cool, still excluding air. Dissolve the melt in about 500 cc. of water, heating gently if necessary. Transfer to a beaker, cool in ice and cautiously add concentrated hydrochloric acid until the solution is acid. Extract repeatedly by shaking with 100 cc. portions of ether in a separatory funnel. Combine the ether extracts and bleach by shaking with animal charcoal. The filtered ether extract should be kept as a stock solution. To prepare the Kreis reagent dilute a portion of the stock solution with ether until it gives a good reaction with a strongly rancid fat but a less intense reaction on further dilution.

Fifteen grams of resorcinol ordinarily yield 10 l. or more of the Kreis reagent. This reagent appears to be a satisfactory substitute for that prepared from pure phloroglucinol.

A COLLOIDAL METHOD FOR INCREASING THE VOLUME OF ADHESIVE WATER-GLASS

By **J. D. Malcolmson**

Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

Received May 28, 1919

Commercial silicate of soda, or water-glass, with a density of about 42° Bé., is used in very large quantities as an adhesive in the fiber container industry. In fact, this material is the only adhesive employed for gluing together the components of both double-faced corrugated board and laminated solid fiber board.

During a recent emergency created by freight embargoes and other war-time causes of delay, the stocks of water-glass in the box-makers' hands began to run low. This laboratory was at that time confronted with the problem of increasing the volume of the 42° Bé. adhesive without injuring its essential properties. These properties, which make water-glass of especial value to the box-board industry, may be classed as follows:

(1) Adhesive value. (A powerful adhesive is not required, but it must be equal to or greater than the "felted" strength of the paper fibers)
(2) Proper viscosity. (This will be discussed below.)
(3) Low penetration. (This prevents loss of adhesive through absorption by the relatively porous corrugated strawboard. This property obviously depends upon the viscosity.)
(4) Fast setting and drying rate. (The boards are run through the pasting machines at a speed of upwards of 60 ft. per min.)
(5) Relative insolubility when dry.
(6) Relative flexibility when dry.
(7) Negligible effect of age.
(8) Relatively low cost. (This is necessary because container board is a product of relatively low cost.)

Water-glass at about 42° Bé. is a fairly viscous liquid. High viscosity is one of its desirable features for use in this industry, and is only limited by the fact that it must be fluid enough to be pumped to various parts of the factory and to flow over the troughs and rollers as fast as needed. High viscosity prevents loss by absorption and insures a satisfactory drying rate and adhesive power. Initial attempts to increase the volume of a given amount of the adhesive were made by diluting with water. This naturally lowered the viscosity to a very marked extent and the drying rate and adhesive power were correspondingly lowered to a prohibitive degree. Much of this adhesive, moreover, was absorbed by the strawboard. These experiments clearly showed that the desirable properties of water-glass as an adhesive are, in general, a function of the viscosity, and as this is lowered these properties suffer proportionately.

The problem was finally solved by diluting the water-glass with brine.[1] It was found possible by this means to increase the volume of the solution by 25 per cent without lowering the original viscosity or detracting from any of the essential qualities of the adhesive as listed above. This process was perfected on a laboratory scale and subsequently tried out on a large scale in several factories. It was found to work satisfactorily, the only disadvantages being:

(1) The possibility of a drop in the market price of water-glass.
(2) The increased floor and storage space required.
(3) The installation of equipment.

Water-glass is a complex mixture including sodium silicate (probably hydrated), water and silica (or silicic acid) in the colloidal state. The actual proportions of Na_2O and SiO_2 to form the compound $Na_2O.xSiO_2$, and the proportion of SiO_2 in the colloidal form, are questions about which much uncertainty still exists. They no doubt vary in different lots of water-glass. Most investigators are of the opinion that the silica is in chemical combination to the extent of Na_2O2SiO_2 and that any excess SiO_2 over this amount is merely "dissolved." Analyses of water-glass are reported in terms of Na_2O, SiO_2 and H_2O. The adhesive grade usually contains from 3.0 to 3.5 parts of SiO_2 to one part of Na_2O.

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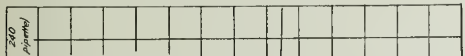
[1] Kerr, This Journal, **10** (1918), 471.

[2] *Ber.*, **12**, 503.

[1] The writer desires to acknowledge his indebtedness to Dr. E. W. Tillotson, Jr., assistant director of Mellon Institute, for his suggestions and assistance in the development of this method.

When an electrolyte is added to water-glass the colloidal SiO_2 is coagulated. This forms what is sometimes termed a "weakly agglutinated gel" which, if undisturbed, soon coalesces to a dense mass. This, of course, is a well-known method of preparing the silicic acid gel, preparatory to dialysis.



APPROX. ANALYSES

SAMPLE	No. 1	No. 2	No. 3	No. 4
GRAVITY (Bé)	41.5°	41.4°	41.5°	43.5°
Na_2O	8.8%	9.0%	9.10%	9.5%
H_2O	61.2%	61.5%	61.5%	60.6%
SiO_2 (By Diff.)	30.0%	29.5%	29.4%	29.9%

FIG. 1—THE EFFECT ON THE VISCOSITY OF WATER-GLASS PRODUCED BY THE ADDITION OF VARIOUS BRINES

If, however, the water-glass solution is stirred during the addition of certain electrolytes and for a short time afterwards, the gel particles do not have a chance to coalesce, but will go back into "solution," *i. e.*, they are "peptized." Fortunately, brine, a cheap and readily accessible reagent, was found to coagulate and peptize the gel in a more satisfactory manner than any of the other more or less cheap solutions experimented with. This peptization of the gel is accompanied by an enormous increase in viscosity over that which results from dilution of the water-glass with an equal volume of plain water.

This final viscosity depends upon the concentration of the added brine, other factors being constant. The volume of most water-glasses can be increased to the extent of 25 per cent by the addition of a brine about two-thirds saturated, and with no loss in viscosity, adhesive power or drying rate. Small increases in the concentration of the brine beyond this point cause proportionately greater increases in the viscosity and the final solution soon loses all fluidity. This is shown graphically in Fig. 1. Twenty parts by volume of brine were added to eighty parts by volume of four different commercial brands of water-glass. All determinations were made at 20° C. All were increased in volume by the same amount with brines of varying concentration. The effect on each sample is distinctly different, yet the analyses of the original samples are so similar that a relation between analysis and the effect of brine is not clearly indicated.[1] This is due, perhaps, to variations in the relative proportion of silica in the colloidal state and would not be indicated by the nature of the analytical method. Owing to lack of time, the samples were not dialyzed, although dialysis would probably account for this action. It will be noticed, however, that the viscosity of all four samples was lowered to the same point by the addition of an equal amount of plain water, regardless of the original viscosity.

Water-glass thickens so rapidly when exposed to the air, and moves so slowly through ordinary viscosimeters, that only "comparative viscosities" were determined. These determinations were made by measuring with a stopwatch the time required for each solution to flow past marks at the top and bottom of the same 20 cc. pipette under constant conditions. This time, in seconds, was recorded as a measure of the "relative viscosity."

It was found in each case that an increase of 25 per cent in the volume of the water-glass was the maximum efficient amount. More brine than this makes the peptization process increasingly difficult, until a concentration is soon reached which entirely inhibits this action.

In practice the adhesive user can easily plot a viscosity curve by treating small lots of his particular supply of water-glass with a set of standard brines of different concentrations. He can then determine the proper brine concentration for reaching that final viscosity which best suits his needs.

The actual treatment is made on a fairly large scale, using mechanical agitators or stirrers. The stirring does not have to be violent but merely enough to keep the liquid in motion. Agitation of a measured quantity of water-glass is started, and the corresponding volume of brine is then added to the mixture in several fine streams. If the brine is added too fast or in too coarse a stream the resulting gelatinous curds are so large that a longer time is required for peptization, due to the smaller surface area presented. When all the salt solution is added the batch has a sticky consistency, but in a few minutes begins to recover fluidity. The stirring must be continued until no more curds are present. On a small scale, 20 to 30 min. suffice, while on a large scale this may have to be increased, depending upon the rate at which the brine was added and upon the efficiency of the stirring operation.

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[1] In attempting to find some such relation it was noticed that when the ratio of SiO_2 to Na_2O was plotted against the concentration of brine necessary to duplicate the original viscosity, the four samples fell approximately on a straight line (Fig. 2). More data would be necessary to establish the significance of this relation. It is no doubt true, however, that as the proportion of Na_2O increases, stronger brines are necessary for reaching the original viscosity. Thus, a fifth sample having a ratio of 2 : 5 (10.65 per cent Na_2O) showed approximately the same final viscosity whether treated with plain water or saturated brine. Water-glasses of comparatively low alkalinity are, on the other hand, extremely viscous even in the original state.

The cost of this treatment is low, since the final increased adhesive only contains from 3 to 4 per cent, by weight, of NaCl. Any ordinary grade of salt seems to work satisfactorily.

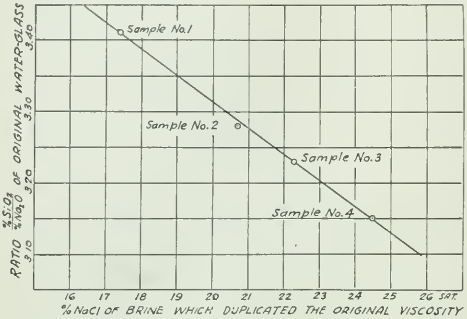

Fig. 2

The final viscosity can be varied to a large extent by small changes in the brine concentration. This is shown by the steepness of the curves in the neighborhood of the "original viscosities." This brine concentration, however, can be controlled very well in practice by the use of a standard hydrometer, since it is not at all difficult to read the latter to one-tenth of a degree, which corresponds to one-tenth of one per cent of NaCl.

The treated adhesive does not seem to be affected by age. Samples out of contact with the air have been kept and observed for over a year and show no appreciable change in adhesive power, and no loss of viscosity. After several months a flocculent sediment often settles out, but this apparently has no effect on the adhesive quality or the viscosity.[1]

Samples of corrugated container board made in both laboratory and factory, with the treated adhesive, also have remained unaffected by age for a period of more than one year.

SUMMARY

I—The desirable properties of water-glass for use as an adhesive are, in general, a function of the viscosity.

II—A method is described of increasing, to the extent of 25 per cent, the volume of adhesive water-glass by the addition of brine, without impairing the viscosity and other desirable properties of the adhesive.

III—This method involves the practical application of certain phenomena of colloid chemistry, such as coagulation and peptization.

ON THE DISTILLATION OF AMMONIA

By B. S. Davisson

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Received August 8, 1919

The distillation of ammonia from an alkaline solution into standard acid and titrating or nesslerizing to determine the ammonia has long been in practice. Many procedures and forms of distilling apparatus have been suggested for transferring the ammonia into the standard acid, but all have one or more objectionable features.

A prolonged study of nitrogen methods made in connection with the biological studies of this laboratory[1] has involved the use of many different kinds of distilling apparatus. Both water- and air-cooled condensers have been used and, while many satisfactory determinations were made with air-cooled condensers, an apparatus suitable for the distillation of ammonia from an alkaline solution into standard acid should possess a water-cooled condenser. The ordinary Kjeldahl distilling rack, although water-cooled, has many undesirable features, especially when small amounts of nitrogen are being determined. The solubility of the soft glass still head and adapter ordinarily used together, with the adsorption of ammonia by the block tin condenser, led to the abandonment of this type of apparatus. The one found most satisfactory for careful research work has been described.[2] It is made of Pyrex glass with only one rubber connection which does not vitiate the results. The scrubbing device for removing entrained alkali is sufficiently satisfactory for use with $N/100$ solutions. This apparatus, however, is not entirely suited for general routine analytical work. A scrubbing device and an adapter have been devised for use with block tin condensers,[3] thereby overcoming the most objectionable features of the ordinary Kjeldahl distilling rack. By using these devices with good tin condensers, proceeding as outlined below, it is easily possible to obtain an accuracy of less than 1 per cent with 5 mg. of nitrogen.

We desire to recommend here that the apparatus as finally adopted, *i. e.*, the all-glass apparatus or block tin condensers with the new scrubber and adapter, be used in connection with the methods described from this laboratory. While the Mitscherlich distilling apparatus was found satisfactory in this laboratory for determining nitric nitrogen, it may not prove equally so in other laboratories. The procedures for using the distilling apparatus, as recommended, in connection with the determination of nitric nitrogen and total nitrogen are given below.

PROCEDURE FOR DETERMINING NITRIC NITROGEN

The procedure[4] previously recommended is followed with the exception of the distilling apparatus, which is replaced by that described above. The cooled condenser is used for the first 20 min. of moderate boiling, after which it is drained and the boiling continued, more rapidly, for 20 min. longer. The receiver is then removed, cooled, and titrated.

PROCEDURE FOR KJELDAHL NITROGEN DISTILLATION

The procedure followed in most laboratories consists in distilling through a water-cooled condenser until about 150° cc. of distillate have been collected.

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[1] This same sediment is observed, to a lesser extent, when samples of ordinary water-glass are kept for some time in bottles, and is probably due to the action of the free alkali on the glass.

[1] This Journal, 7 (1915), 521; 8 (1916), 896; 10 (1918), 600; 11 (1919), 306; *Ann. Mo. Bot. Gardens*, 6 (1919), 1.

[2] *Ann. Mo. Bot. Gardens*, 6 (1919), 45.

[3] This Journal, 11 (1919), 465.

[4] *Loc. cit.*

The major portion of the ammonia passes over in the first few minutes but the prolonged distillation is necessary in order to remove the last traces of ammonia from the condenser. Benedict[1] found that the last traces of ammonia could be rapidly removed from the condenser by steaming for a short time, thereby lessening the time necessary for a distillation. He recommends draining the condenser after 15 min. of boiling and continuing the boiling until the receiving solution is slightly warmed.

Benedict's recommendation has been followed for two reasons, both to remove quickly the last traces of ammonia from the apparatus, and to keep the volume of solution in the receiver as small as possible, *i. e.*, about 110 cc., in order to reduce the hydrolysis of the indicator salt. The length of time of a distillation recommended by Benedict was found to be insufficient to remove the last traces of ammonia from the boiling solution. We have, therefore, adopted a different procedure. The solution is distilled slowly for the first 20 min. with cooled condenser, during which time about 80 cc. of distillate are collected. The condenser is then drained and the distillation continued for 15 min. longer with somewhat more rapid ebullition. The receivers are then removed, covered to prevent the absorption of carbon dioxide, cooled and titrated.

During the slow distillation with the cooled condenser the ratio of ammonia to steam passing over is much greater than with rapid boiling, yet the rate of distillation of ammonia is about the same. The steam passing over after the condenser is drained condenses in the receiving solution until the acid solution becomes hot, after which it passes out of the solution thoroughly scrubbed of any ammonia which it carried. That the ammonia is completely recovered by this method of distillation is shown by the data in Table I. The figures were obtained by digesting pure solutions of ammonium sulfate with 15 cc. of concentrated sulfuric acid, 0.5 g. copper sulfate, and 5 g. of potassium sulfate and distilling with 50 cc. of strong alkali (ammonia-free) into $N/50$ acid. The volume of solution in the receiving flask is kept small by this method of distillation and at the same time the solution in the distilling flask is not reduced in volume. The above procedure has been found entirely satisfactory for the amounts of nitrogen which are encountered in total nitrogen determinations.

TABLE I—THE RATE OF DISTILLATION OF AMMONIA
(Nitrogen Taken—5.045 Mg.)

CONDENSERS COOLED		CONDENSERS DRAINED	TOTAL
First 10 Min. Mg.	Next 10 Min. Mg.	Next 15 Min. Mg.	35 Min. Mg.
3.872	0.990	0.177	5.039
4.513	0.546	0.033	5.092
4.618	0.456	0.106	5.030

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[1] *J. Am. Chem. Soc.*, **22** (1900), 259.

ADDRESSES AND CONTRIBUTED ARTICLES

A REVIEW OF THE LITERATURE OF EMULSIONS[1]

By Arthur W. Thomas

DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK, N. Y.

Emulsions have been the subject of lively comment in chemical literature for the past twenty years. No general theory for emulsification has been elucidated, although many have been proposed from time to time, only to be shown subsequently to apply to special cases. There has accumulated, however, a mass of arbitrary data which can be profitably applied.

An emulsion is a heterogeneous system consisting of one liquid dispersed as tiny droplets in another liquid. It has been definitely established that three phases are essential for the formation of a stable emulsion: (1) Liquid A, (2) Liquid B, and (3) an emulsifying agent. The two liquids must be immiscible, or nearly so, in one another. The common types of emulsion are those wherein water constitutes one of the liquid phases, and we recognize two main types: (1) A liquid (oil, for instance) dispersed in water, and (2) water dispersed in oil. The factor which controls the type of emulsion, *i. e.*, whether water or oil is the external phase, is the nature of the emulsifying agent.

In general, if the emulsifying agent is more easily wetted by water than by oil, then water will be the external phase and oil the dispersed phase, while if the emulsifier is more easily wetted by oil than by water, the reverse will be true. Or, as Bancroft[2] puts it: If the surface tension between Liquid A and the emulsifying agent is lower than the surface tension between Liquid B and the emulsifying agent, Liquid A will be the dispersing and Liquid B the dispersed phase. Since the emulsifying agent is almost always recognized as a colloidal substance, it is fairly safe to say that a hydrophile colloid as emulsifying agent will emulsify oil in water and a hydrophobe colloid will emulsify water in oil. This latter statement is subject to modification, however, which will be considered later.

There is a very simple and reliable method of determining the type of emulsion. Upon addition of an emulsion of oil-in-water (*i. e.*, oil dispersed phase and water external phase) to water, it will disperse. Similarly, a water-in-oil emulsion will mix with oil. In short, an emulsion will freely mix or dilute with more of its external phase, but not with more of its internal phase.

Robertson[1] suggested a method of staining with Soudan III (a fat-soluble dye). He stated that if Soudan III is sprinkled upon the surface of an oil-in-water emulsion the red color will be confined to the oil droplets and a mass of discontinuous red specks will result, whereas when sprinkled on the surface, a water-in-oil system will become uniformly red. This test has lately been severely criticized, and it has been shown that Robertson was led into misinterpretation of his olive oil-water-NaOH emulsions. He claimed to show critical concentrations leading to emulsions of water-in-oil. This has since been shown to be highly improbable.

OIL-IN-WATER EMULSIONS

There are three main classes of this type of emulsion:

(1) The emulsifying agent is an electrical charge on the oil particles, probably due to selective adsorption of the OH^- ion of water by the oil particles.
(2) The emulsifying agent is a water-soluble colloid.
(3) The emulsifying agent is an insoluble, or very slightly soluble colloid.

There are many cases also where a combination of two or even three of the above may function as emulsification agents.

(1) ELECTRICAL CHARGE AS EMULSIFYING AGENT—These emulsions are the simplest. They are identical with those observed

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[1] Read at the December 5, 1919, Meeting of the New York Section of the American Chemical Society, Chemists' Club, New York, N. Y.

[2] *J. Phys. Chem.*, **17**, (1913), 501.

[1] *Kolloid-Z.*, **7** (1910), 7.

in the condensate from steam engines. They may be prepared in any of three ways.[1]

(*a*) By shaking a small amount of mineral oil (2 cc.) with a larger volume of water (100 cc.) for 48 hrs.

(*b*) By boiling a drop of mineral oil with excess water under a reflux condenser for 30 hrs.

(*c*) When a small amount of mineral oil dissolved in alcohol is poured into water an emulsion results immediately.

Lewis found the size of the particles in these emulsions to be alike no matter how made, and of the order of 0.4 micron. They are negatively charged, the potential difference of the double layer (Helmholtz effect) being —0.05 volt. His measurement of the size of the charge on the droplets, by electrophoresis method, indicated 4.4×10^{-7} electrostatic units. These emulsions owe their stability to the electrical charge and Brownian movement.

The origin of this electrical charge is obscure. Ellis[2] ascribed it to difference in dielectric constants, according to the rule of Coehn that a substance of high dielectric constant is positive to one of a lower dielectric constant when one is dispersed in the other. This, to be sure, does not explain. He prepared mineral oil emulsions by the shaking method and obtained a concentration of one part oil in 10,000 parts of water, the size of the particles being 1 to 2 microns in diameter, and the specific conductivity of the emulsion was 18×10^{-6} mhos. He found the potential of the double layer to be —0.05 volt, as Lewis did; but his measurement of electrical charge showed 2.12×10^{-6} electrostatic units for the 1-micron particles. He also noted that they were most stable in the presence of $N/1000$ sodium hydroxide. He ascribed the stability of this type entirely to the electrical charge and stated that surface tension had nothing whatever to do with it.

Hatschek[3] suggested that the stability of such mineral oil emulsions might be due to the fact that the specific gravities of the phases were close to each other, but Groschuff[4] contested this view.

Powis[5] prepared this type of emulsion by the shaking method and determined the double layer potential to be —0.046 volt, which checks fairly well with Lewis and Ellis. He studied the effect of addition of electrolytes to the emulsion and noted that anions have the power to increase this negative potential, while cations decrease it. Very small amounts of KCl and $K_4Fe(CN)_6$ (up to 0.001 molar) increased it, while larger amounts decreased it. Salts with polyvalent cations always decreased it, due to the predominating positive charge of the cations over the anions. He noted later[6] that while an immediate sharp change in the contact potential occurred upon addition of salt, there always ensued a secondary slower change; in the case of a salt like $BaCl_2$ the change is continuous in the same sense, whereas in cases like $AlCl_3$, it reverts back a little, due to loss of Al^{+++} on account of hydrolysis. Powis' studies on coagulation of these emulsions by means of electrolytes will be discussed later.

(2) WATER-SOLUBLE COLLOID AS EMULSIFYING AGENT—Good emulsifiers of this class are sodium and potassium soaps, egg albumin, gelatin, glue and other water-soluble proteins, gum arabic (acacia), gum tragacanth, Irish moss, milk, starch saponin and quillaia bark extract.

Previous to 1899, NaOH was classified as an excellent emulsifying agent for fatty oils in water, but Donnan's[7] investigation showed that its emulsifying powers were really due to the soap formed by interaction with the small amount of free fatty acid that is always present in fatty oils. He proved this by means of the drop number method, and stated that those fatty acid salts which greatly lower the surface tension are good emulsifiers, and that since they lower the surface tension they must concentrate in the surface layers about the droplets of oil, and since the soap layer is still more concentrated at the points of contact, where bubbles might happen to come together, capillary forces tend to separate them.

In a later work, Donnan and Potts[1] measured the drop numbers of aqueous solutions of the sodium salts of the fatty acids. They noted that all lowered surface tension, the lowering increasing with the higher molecular weights, but that it is strongly evident first with sodium caprylate. Emulsifying powers are not evident with this salt, but commence with sodium laurate. The emulsifying power increases with increase in concentration to $N/300$ soap solution, above which it decreases, due to the coagulating effect of Na^+ ions.

They objected to Pickering's theory (see later) and stated that stability of emulsions is due partly to the electrical charge and partly to presence of surface tension lowering substances which, according to the theories of Willard Gibbs, must concentrate in the surface layer.

A classic study of emulsions was published by Pickering[2] in 1907. He pursued his investigations in order to make a suitable germicidal spray for agricultural purposes. In all his experiments he emulsified a paraffin oil in water, by pumping it back and forth through a rose-nozzle garden syringe. He found potash soaps to be better than sodium soaps as emulsifiers and noted that a certain critical concentration of soap was required for each proportion of oil and water, *e. g.*, to emulsify 75 volumes of oil with 25 volumes of water, the latter must contain 0.7 to 1.8 per cent potash soap. For 40 volumes oil to 60 of water, 0.3 to 25 per cent soap can be used.

He noted that soaps vary greatly in emulsifying power, some brands being useless and, in fact, two batches of the same brand may vary greatly in emulsifying power. He noted also that while rise in temperature facilitated emulsification, it had no influence on the composition.

Pickering's 70 to 80 per cent oil emulsions were viscid like thick cream, even when benzine was used. Size of particles was about 0.1 micron. He succeeded in emulsifying 99 cc. of paraffin oil in 1 cc. of 1 per cent potash soap solution by successive additions of small portions. This famous emulsion was pure white and as stiff as a blanc-mange. It could be diluted with water but not with oil, hence was of the oil-dispersed-in-water type.

He noted that his strong emulsions were poor conductors of heat. It is possible to boil a beaker of such an emulsion at 160° to 170° C. for several minutes, while the center remains at less than 100° C. When kept in closed vessels they were permanent for months, but cracked soon after exposure to *dry* air. Strange to say, his emulsions generally separated, no matter what the starting composition, to form a permanent 65 to 82 volume per cent emulsion of oil in water.

Five emulsions of "Solar distillate" (a paraffin oil distilling between 240° and 350° C.) were prepared by Pickering, as follows:

SAMPLE	Oil Vol.-Per cent	Soap Solution Per cent
1	67	1
2	50	1
3	33	1
4	50	5
5	50	0.2

After standing 12 wks. they had all separated into emulsions containing from 72 to 82 per cent oil (as emulsion) in the upper layer and water below. Analysis showed a steadily decreasing oil content in the emulsions from the top downwards. In each case one-quarter of the column of emulsion from the top deviated but slightly from 84.5 per cent oil. The effect of decreasing the soap percentage is to increase the size of the globules finally to a point where permanence is no longer possible. Pickering reported some novel effects with solid emulsifying agents which will be discussed under that heading later. Of the water-soluble emulsifiers he stated that soap is the best and that dissolved starch, milk and flour are good, although the last named gives a flocculent rather than a creamy emulsion and milk forms solid clots. Glue is good. Egg albumin is good but gives rather frothy effects owing to inclosing air bubbles. Saponin and quillaia bark are good if proportion of oil is small.

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[1] Lewis, *Kolloid-Z.*, **4** (1909), 211.

[2] *Z. physik. Chem.*, **78** (1912), 321.

[3] *Kolloid-Z.*, **9** (1911), 159.

[4] *Ibid.*, **9** (1911), 257.

[5] *Z. physik. Chem.*, **89** (1914), 91.

[6] *Ibid.*, **89** (1914), 179.

[7] *Ibid.*, **31** (1899), 42.

[1] *Kolloid-Z.*, **7** (1910), 208.

[2] *J. Chem. Soc.*, **91** (1907), 2001.

In 1912 Newman[1] reported results of attempts to emulsify water and benzene, using oleates. He found that when benzene and water are emulsified by sodium oleate, water is always the external phase and that it is possible to make homogeneous emulsions up to 0.5 per cent benzene, and from 80 to 90 per cent benzene. Failure to make the intermediate emulsions, he ascribed to his method of shaking. He made a stiff jelly with 99 cc. benzene and 1 cc. water, using 0.05 g. sodium oleate. This emulsion was stable for more than 6 wks. With his shaking machine it was possible to get concentrated emulsions only by gradual addition of the liquid which is to be the internal phase.

Briggs[2] measured the amount of sodium oleate adsorbed by benzene emulsions in water and found that the amount of soap adsorbed increases with the degree of dispersion of the benzene particles. He constructed an ingenious laboratory type of homogenizer for the preparation of his emulsions.

In a subsequent paper[3] Briggs and Schmidt found that the drop number test cannot be used to judge the power of an emulsification agent for benzene in water. While 1 per cent solutions of both gum arabic and gelatin gave lower drop numbers than water when benzene was run into these solutions from a drop pipette, still the gum and gelatin will emulsify benzene in water, due, no doubt, to the elastic semi-solid films which they form around the benzene droplets. They are not as good as soaps, however. The optimum amount of soap to form a good emulsion was found to be 0.01 per cent of the total volume.

Fischer's[4] theory of emulsions is that a hydration compound is essential, *i. e.*, the oil globules must be covered with films of a hydrated colloid. He evidently is not familiar with the lubricating oil emulsions of Lewis, Ellis, Powis and Hatschek, nor with the solid emulsifying agents of Pickering.

Roon and Oesper[5] and later Crockett and Oesper[6] studied emulsions used in pharmaceutical practice. By the trituration-in-a-mortar method they learned that it is best to add the proper amount of water to the internal phase and the emulsifier and then triturate, and that it is best to form an emulsification nucleus in this manner, which can be modified afterwards. The proportions giving the best results are 4 parts of oil, 2 of gum arabic, and 3 of water. This nucleus is miscible in all proportions with water. Nuclei of one composition act as stabilizers for incomplete emulsions of other compositions and nuclei of one composition act as emulsifiers for other internal phases. They found Irish moss and gum tragacanth to be good emulsifiers, with the exception that tragacanth cannot be used with turpentine and forms unmanageable masses with fatty oils. They say "traces" of soap crack Irish moss emulsions, while they aid gum arabic emulsions. They are inclined to accept Fischer's hydration theory.

Davey,[7] in searching for a substitute for organic solvents in Japan varnish, found that he could emulsify linseed oil with water by addition of ammonium hydroxide and slowly stirring in a closed heated receptacle. He made the interesting discovery that such emulsions scum when exposed to air containing carbon dioxide at 17° C. or higher, but not when exposed at 16° C. or lower, or to air free from carbon dioxide at any temperature. The particles of dispersed phase were negatively charged. This emulsion proved to be a good paint.

(3) INSOLUBLE OR ONLY SLIGHTLY SOLUBLE COLLOID AS EMULSIFYING AGENT—Tfol[1] reported that Arabs in Northern Africa used an argillaceous earth as a substitute for soap in washing linen. He found that this earth readily emulsified oils in water.

Pickering[2] was probably the first to study the efficacy of certain solids as emulsification agents. He found that basic copper sulfate (made by adding 1 part of CaO to 7 parts $CuSO_4.5H_2O$) in solution in water is an excellent emulsifier. At least one part of $CuSO_4.5H_2O$ converted to the basic salt is needed to emulsify 120 parts of paraffin oil. Immediate and stable emulsification results by one stroke of the syringe and the product is very efficient as a germicidal spray in agriculture. These emulsions resembled his potash soap emulsions in all properties, except that the stable layer contained about 40 per cent oil. The ratio of CuO to emulsified oil was fairly constant, about 0.92 part of CuO to 100 parts of oil. His experiments with other solid substances yielded results as classified below.

Substances which emulsify—Basic ferrous sulfate, basic copper sulfate and basic nickel sulfate are the best. Ferrous and ferric hydroxides are good. Basic zinc and basic aluminum sulfates give good emulsions temporarily. The precipitate formed by adding sodium carbonate to copper sulfate is good. Calcium carbonate and arsenate are good when freshly precipitated but they soon become crystalline and de-emulsification follows. Lead arsenate and some unheated fine clays are good. Iron sulfide is good for small amounts of oil and zinc oxychloride is fair.

Substances which produce quasi-emulsions—Lime, silica, alumina and plaster of Paris, dried, and the following when freshly precipitated, act: Basic cadmium sulfate, magnesium hydroxide, copper hydroxide, basic zinc and aluminum sulfates, tin oxychloride, lead arsenate paste, copper sulfide, iron sulfide.

Little or no emulsifying power—Precipitated lead chloride, lead sulfate, barium sulfate, silica hydrosol, sulfur, flowers of sulfur, Paris green, alcoholic solution of rosin precipitated by water, ferrous ferricyanide, ferric ferrocyanide and purple of Cassius. In these cases the oil seems to wet the precipitates more than water does.

Later Pickering[3] stated that while high viscosity and low surface tension of a liquid facilitates the emulsification of an oil in it, yet it is possible to make an emulsion in a liquid which does not possess these properties. The most important condition is the presence of small particles insoluble in the dispersion medium which coat over the oil particles and prevent them from coalescing. In order that such particles have the power to form emulsions they must show only a slight tendency to unite with one another, must be readily wetted by water and must not be crystalline. He also made the novel discovery that potassium cupric tartrate will emulsify a mixture of alcohol and water. If this salt be added to an aqueous solution of alcohol, it will cause the water and alcohol to separate into two layers. Agitation results in emulsification.

Hofmann[4] used silver dichromate to emulsify chloroform in water.

In 1915, Briggs and Schmidt[5] found that colloidal ferric hydroxide (formed by hydrolysis of ferric acetate solution), was a fairly good emulsifier for benzene in water.

WATER-IN-OIL EMULSIONS

Calcium and aluminum soaps are used in lubricating greases. Holde[6] published a discussion of these greases in 1908. They are solutions of lime soaps (15 to 23 per cent) in heavy mineral oil with 1 to 4 per cent water emulsified in them. Some American lubricating greases, especially for automobiles, consist of aluminum soaps dissolved in mineral oils with water emulsified in them by the aid of rosin.

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[1] *J. Phys. Chem.*, **18** (1912), 34.

[2] *Ibid.*, **19** (1915), 210.

[3] *Ibid.*, **19** (1915), 479.

[4] *Science*, **43** (1916), 468.

[5] THIS JOURNAL, **9** (1917), 156.

[6] *Ibid.*, **9** (1917), 966.

[7] *Physical Review*, **11** (1918), 138.

[1] *Pharm. J.*, [4] **6** (1898), 1228.

[2] *Loc. cit.*

[3] *Kolloid-Z.*, **7** (1910), 11.

[4] *Z. Biol.*, **63** (1914), 395.

[5] *Loc. cit.*

[6] *Kolloid-Z.*, **3** (1908), 270.

Bancroft[1] states that lanolin is an emulsion of water (22 to 25 per cent) in wool wax and that it is possible to emulsify as much as 80 per cent water in wool wax. The writer believes that this may be due to the cholesterol which wool wax contains. These emulsions are stable for years.

Newman[2] found that while sodium oleate emulsifies benzene in water, magnesium oleate emulsifies water in benzene. He stated that it is never possible to emulsify water in an oil by means of sodium soaps, contrary to Robertson's findings. By using proper procedure he succeeded in emulsifying 96 per cent water in benzene. The stability is increased by the addition of a little sodium oleate. He stated that in mixed paints water is dispersed in the oil and that this is due to the presence of rosin as an emulsifying agent, and not to the pigments. In conclusion he presented his theory that whether one liquid is emulsified in another or not depends upon the emulsifying agent. A hydrophile colloid will tend to make water the external phase, while a hydrophobe colloid will tend to make water the internal phase and the colloid must be able to make a suitable coherent film around the globules to be an emulsifying agent.

Briggs and Schmidt[2] found that for the emulsification of water in benzene, magnesium oleate is fair (forms quasi-emulsions finer than aluminum palmitate). Magnesium resinate, copper resinate and lead oleate are unsatisfactory. Aluminum palmitate forms quasi-emulsions.

Clowes[3] has performed some striking experiments with soap emulsions of olive oil and water. By addition of calcium chloride to an emulsion of oil in water (with sodium oleate as emulsifying agent), when the calcium concentration exceeds the chemical equivalence to sodium, the emulsion passes through a critical point and changes to water dispersed in oil. He found that sodium, potassium and lithium soaps emulsify oil in water while magnesium, strontium, barium, iron and aluminum soaps emulsify water in oil. The first series of soaps are soluble in water and not in oil, while the second series are soluble in oil but not in water. The alkali soaps are wetted more by water than by oil and since it is thought that the surface tension is lower on the water side than on the oil side of the globules, the film will bend convex to the water and concave to the oil, enveloping the oil articles, because the area of the inner surface of a sphere is less than that of the outer surface. Similar reasoning holds for the dispersion of water in oil by the other soaps mentioned.

Clowes illustrates this phenomenon by the accompanying diagram.

In 1918 Schlaepfer[4] reported his experiments with carefully purified carbon black (gas black, soot) as emulsifying agent. This substance must be wetted more by oils than by water, because in all cases he obtained dispersions of water in the oil and never oil in water. As dispersion media he used kerosene, turpentine, benzene and toluene. With 60 cc. kerosene, 240 cc. water and 1.5 g. soot, he obtained an almost solid emulsion.

Moore[5] checked Schlaepfer's results. He was able to emulsify water and ammonium chloride solutions in kerosene with lamp black. Highly calcined lamp black and petroleum coke would not function as emulsifying agents. As the concentration of the ammonium chloride solutions was increased, the drops grew larger, due to high surface tensions of the solutions. He found that water wets raw lamp black more readily than extracted lamp black, while normal ammonium chloride solutions wet raw lamp black more readily than purified lamp black.

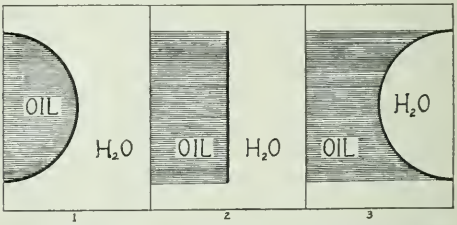
BREAKING OF EMULSIONS

In general, de-emulsification can be accomplished by:

1—Addition of excess of dispersed phase.
2—Addition of a liquid in which the two liquid phases are soluble.
3—Destruction of the emulsifying agent.
4—Filtration.
5—Heating.
6—Freezing.
7—Electrolyzing.

The problem of breaking mineral oil emulsions in steam engine condensates has interested engineers for a long time.

Hatschek[1] offered a solution of the difficulty in a filtration method. He found that such emulsions when filtered through *amorphous* $MgCO_3$ or $CaCO_3$ (causticizing mud) came through free from oil. On a 4.5-sq. ft. filtering surface covered 0.125 in. thick with amorphous $CaCO_3$ he was able to filter 30 cu. ft. per hr. under 10 lbs. per sq. in. pressure. The adhering oil broke loose from the filtering surface and floated to surface. The permeability of the filter was but slightly diminished after 6 hours' filtration. He advises using the $CaCO_3$ in a filter press at not higher than 50 lbs. pressure because higher pressures squeeze the emulsified oil drops between the interstices in the filter bed.



EMULSIFYING AGENT OR FILM	EMULSION FORMED
(1) Sodium oleate alone or sodium oleate in excess of calcium oleate equivalent	Oil in water
(2) Chemically equivalent proportions of sodium oleate and calcium oleate	Critical point
(3) Calcium oleate alone or calcium oleate in excess of sodium oleate equivalent	Water in oil

This method worked also for emulsions of kerosene, petroleum oils, fatty oils, etc., where soap or saponin had been used as emulsifiers.

He also mentions that addition of alum and alkali, and also passing oily water between iron electrodes works well. Ferric hydroxide is formed at the anodes and combines with the oil particles and coagulates them. These methods do not appear to be practicable for commercial use.

For laboratory purposes, Hatschek recommends the ultrafilter, using Bechhold's 5 per cent collodion papers, as highly satisfactory.

In 1911 Hatschek[2] tried hydrochloric acid and sodium sulfate as coagulators. At, or near, the isoelectric point the particles did coalesce to form larger ones (about 3 microns diameter), but oil particles of even this size rise very slowly, about 2 cm. in 48 hrs.

Ellis[3] showed that these emulsions are most stable in presence of $N/1000$ NaOH; and least stable in presence of $AlCl_3$ (0.00022 g. molar); $CuCl_2$ (0.004 g. molar); NaCl (0.16 g. molar).

Powis[4] showed that greatest instability of these emulsions was attained when the contact potential reached ± 0.03 volt. This potential was found in the presence of

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[1] *J. Phys. Chem.*, **17** (1913), 501.
[2] *Loc. cit.*
[3] *J. Phys. Chem.*, **20** (1916), 407.
[4] *J. Chem. Soc.*, **113** (1918), 522.
[5] *J. Am. Chem. Soc.*, **41** (1919), 940.

[1] *J. Soc. Chem. Ind.*, **29** (1910), 125.
[2] *Kolloid-Z.*, **9** (1911), 159.
[3] *Z. physik. Chem.*, **80** (1912), 597.
[4] *Ibid.*, **89** (1914), 186.

KCl, 51 millimolar	$AlCl_3$, 0.02 millimolar
$BaCl_2$, 1.9 millimolar	$ThCl_4$, 0.007 millimolar

A slight increase over these concentrations charges the particles with positive electricity and they become stable again.

In 1914 Ellis[1] showed that colloidal ferric hydroxide from 0.0017 to 0.0039 per cent final concentration coagulates this type of emulsion. Higher concentration results in reversal in charge of the dispersed phase and stability ensues.

Philip[2] advised that the emulsification tendencies of a lubricant be tested before using. He found that very slight contamination of a good nonemulsifying mineral oil by Mexican, Trinidad or Persian crude oils greatly increased the tendency to emulsify. He described a test for the purpose.

Harris[3] proposes to break emulsions of water and petroleum oil by passing a heavy electrical current. The electrodes must be close together.

Dijxhoorn[4] removes emulsified lubricating oil from condenser water by passing 110-volt current through the water as it passes through the feed water pipe.

Rogers[5] breaks emulsions of mineral oil and water by adding sodium salt of a sulfonated mineral oil (0.25 to 4 lbs. per barrel of mixture) and heating.

McKibben[6] passes emulsion of petroleum and water (heated sufficiently to produce vaporization) through an intensified electrical field. The vapors are condensed and cooled and the water drops out.

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[1] *Z. physik. Chem.*, **89** (1914), 145.
[2] *J. Soc. Chem. Ind.*, **34** (1915), 697
[3] U. S. Patent 1,281,952 (1919).
[4] *Le Popier*, **22** (1919), 53.
[5] U. S. Patent 1,299,385 (1919).
[6] U. S. Patents 1,299,589 and 1,299,590 (1919).

McNear and Bowles[1] have patented an apparatus for electrical treatment of emulsions.

Attempts have been made to precipitate emulsified water in linseed oil, etc., by high tension electrical discharge, but so far as can be learned the method has not been perfected. The sparks tend to jump over the surface rather than through the mixture.

Pilat and Piotrowski[2] favor heat treatment under pressure for breaking of crude petroleum emulsions consisting of oil, salt water and earthy matter. In closed kettles holding 40,000 kg., the crudes were heated by steam to 120° to 130° C. at 3 to 3.5 atmospheres pressure. A practically quantitative separation took place in 5 hrs. at 3 atmospheres pressure. The separation was accomplished more quickly at higher pressures.

Koetschau[3] claims that by heating Roumanian and Galician petroleums to 120° to 130° C., the emulsions broke within a few hours. He recommends heating acidified distillates with steam at 3 to 4 atmospheres pressure.

Newman[4] found that emulsions of oil-in-water with soap as emulsifying agent are irreversibly broken by freezing.

One could continue indefinitely discussing special means of breaking emulsions, but from a knowledge of the nature of a given emulsion and application of the principles laid down at the head of this chapter, one ought to be able to deal with each special case.

Since foams are closely related to emulsions it is of interest to note here that Fiske[5] has found isoamyl valerate to be an excellent inhibitor of foaming. He describes methods of preparations of this ester.

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[1] U. S. Patent 1,297,378 (1919).
[2] *Petroleum*, **13** (1918), 1045.
[3] *Z. angew. Chem.*, **32** (1919), 45.
[4] *J. physik. Chem.*, 18 (1914), 34
[5] *J. Biol. Chem.*, **35** (1918), 411.

FOREIGN INDUSTRIAL NEWS

By A. McMillan, 24 Westend Park St., Glasgow, Scotland

FUEL DEPOSITS IN ESTLAND

According to an article in *Engineering*, Estland seems to be better off than most of her neighbors as regards fuel. Large deposits of shale extend from the coast to Wegenberg over an area 80 versts long by 10 versts wide, containing an amount estimated at 1,500,000 tons. The shale contains so large a percentage of oil that it burns if a light is applied. It is being used for the production of gas and electricity in Reval and also for factories and private houses. Preparations are also being made for its application in the driving of locomotives. In the powdered state it is used for firing boilers and is said to give satisfaction. While its calorific value i from 50 to 60 per cent that of coal, its cost is only one-fourth that of coal. The deposits are being worked by the Estnian state and are also attracting attention in England.

SULFURIC ACID MANUFACTURE

A short account of the effective "Grillo" plant erected in England by the government for the manufacture of sulfuric acid by the contact process is given in the *Journal of the Society of Chemical Industry* for October 15. The catalyst employed is platinum, deposited on granules of calcined magnesium sulfate in the proportion of 0.3 per cent. The purified gases from the sulfur burners heated to about 350° C. are passed through two converters in parallel, each containing 10,000 lbs. of the platinized mass distributed on four trays. For absorbing the trioxide produced, towers packed with quartz are used and practically perfect absorption can be obtained. The purification of the gases, which is important in preventing deterioration of the catalyst, is effected by passing the cooled vapors through coke columns and sulfuric acid drying towers; arsenic is thus eliminated and less than 0.02 per cent of other impurities (water and inert dust) retained. Details of efficiency and production-costs are given.

GROWTH OF FRENCH CHEMICAL INDUSTRY

According to *Schweiz. Chem. Zeit.*, September 10, 1919, the French chemical industry has developed greatly during the war. The annual output of sulfuric acid was doubled, increasing from 1,000,000 to 2,000,000 tons. The output of nitric acid per month is three times greater than the total annual output of pre-war days. The yearly output of cyanamide has increased from 8,000 tons in 1913 to 100,000 tons at the present time. Prospects are favorable for the absorption of the surplus war products for agricultural purposes, and viniculture should benefit in particular. Copper sulfate is indispensable in the vine industry and of the yearly output of 50,000 tons, 40,000 tons are absorbed by viniculture. The necessary copper, which is mined in Spain, is, however, controlled by English interests.

JAPANESE CELLULOID INDUSTRY

According to the Japanese press, the following developments are taking place in the celluloid industry: Several Japanese business men have been asked to join in promoting a concern for the amalgamation of the 130 small celluloid factories in Tokyo, the new concern to be capitalized at $1,000,000. Another proposal by a prominent Japanese factory owner is for the formation of a concern with a capital of about $6,000,000, which is to amalgamate the present factory owned by him and the Sakai and the Abosh factories, the capital to be increased to $7,500,000 when and as necessary. The scheme will be extended to cover all the factories in the country. Another version of the proceeding is that eight large firms are to amalgamate shortly. The joint concern is to be called the Dai, Nippon Seruroido Kubushika Kaisha, and its capital is to be $6,250,000.

ARSENIC COMPOUNDS

At a recent meeting of the Chemical Society, London, Prof. F. L. Pyman described a number of arsenic compounds which had been prepared with the hope that they might be used for direct intravenous injection in simple aqueous solution and so replace the elaborate technique required in the administration of salvarsan. These compounds are arseno-benzenes of a new type obtained by the reduction of benzodiazolearsinic acids, which are produced by the action of acetic or formic acid on diaminophenylarsinic acid and its homologs. The new arsenobenzenes form dihydrochlorides which are soluble in water, but, although weaker in acid properties than salvarsan, they still prove too acid for direct intravenous injection. These experiments, says *Nature*, **104**, 342, are, however, of considerable value, as they form a starting point for further work on the replacement of amino groups by heterocyclic nuclei in arsenobenzenes.

INDUSTRIAL SYNTHETIC AMMONIA

According to an article in *Compt. Rend.*, 168 (1919), 1001, the chief object for the fixation of nitrogen in peace times is the manufacture of fertilizers. Ammonia itself cannot be assimilated by the soil, while the nitrate is expensive and the sulfate requires the use of sulfuric acid. According to G. Ville, ammonium chloride is at least equal to the sulfate as a fertilizer and is less heavy than the sulfate. In the Solvay process the ammonia is recovered by the use of lime, but the lime and calcium chloride are wasted. By a new process both the sodium bicarbonate and the ammonium chloride can be precipitated, thus the chlorine and lime are no longer lost and a good transportable fertilizer gained from synthetic ammonia in addition to three tons of sodium carbonate per ton of fixed nitrogen.

FREEING FATS AND OILS FROM METALLIC IMPURITIES

According to a German patent, the contaminated fats are treated with aqueous solutions of the lower organic acids or their salts which are capable of forming complex salts with the metallic impurities, the fats, etc., being oxidized or reduced by the reaction. For example, contaminated maize oil is dissolved in benzine or hydrocarbons and treated with a 5 per cent oxalic acid solution, and the mixture warmed to 90° C. and well mixed by stirring. At the end of 4 hrs. the emulsion is left in the warm until the oil and acid liquors have separated, the latter being then drawn off. The oil, which formerly was dark in color and malodorous and contained 0.1 per cent ash is now light brown, of agreeable odor and taste, and free from ash. Lactic, tartaric, citric, glycolic acid, or glycocoll, or their salts, may be used.

NICKEL-IRON ACCUMULATORS

Arrangements have been made with Batteries (Ltd.), Redditch, to manufacture in England the nickel-iron-alkaline electric accumulator for which Dr. V. Jungner, a Swede, took out his first patent in 1899, and which began to be manufactured on a large scale by a Swedish company about eight years ago. The active material of the positive electrode is nickel hydroxide, mixed with other ingredients, to increase the conductivity. The composition is formed into briquettes which are fed between two inactive perforated nickeled steel strips. The strips are cut up into suitable sizes, folded together and fitted into a steel frame, the complete electrode being then put through a rolling process to ensure perfect contact between the active material and the steel strips. At the same time grooves are formed on the plate to keep the Para rubber insulators in position. The negative electrodes are constructed in the same way, the active material being iron oxide specially prepared and mixed with other materials to prevent self-discharge of the cell. The assembled positive and negative plates are immersed in a solution consisting chiefly of potassium hydroxide, contained in a steel cell with brazed joints. The batteries are made in two types, one for a normal slow discharge in 8 hrs., and the other for rapid discharge in 4 hrs. The average working voltage is 1.2 volts; it drops slightly during the first 15 min. of discharge and then remains practically constant until the cell is discharged.

MANIHOT SEED AND OIL

The manihot, a well-known rubber plant found in Brazil, has not hitherto been considered as a very valuable source of vegetable oil. The Germans in their desperate search for oil from any quarter have turned their attention to this plant. They planted large areas of manihot in German East Africa for the production of rubber and they now propose to consider seriously the possibility of obtaining oil from the plant. Analyses of three varieties of manihot gave the following percentages of shell and oil:

	M. glaziovii Per cent	*M. dichotoma* Per cent	*M. pianhyensis* Per cent
Shell; Kernel	73.25; 26.75	68.25; 31.75	74 25; 25.75
Oil in kernel	41.34	46.14	48.95
Oil in whole seed	11.06	14.65	12.60

Technical manihot oil was prepared from a mixture of 67 per cent *dichotoma*, 30 per cent *pianhyensis*, and 3 per cent *glaziovii* unshelled manihot seeds, the yield by extraction being 13 per cent. On the basis of figures given above, the theoretical yield should amount to 14.15 per cent, and an analysis of the residue showed an oil content of 1.3 per cent. The fatty acids are hard and of brown color. This technical or unrefined oil is used for the manufacture of varnish and soap. The residual cake is said to be a valuable cattle food.

MENTHOL AND PEPPERMINT MARKET IN JAPAN

According to a report from Tokyo, the menthol and peppermint market has become very dull and prices are still strikingly high. The amount exported is also decidedly lower. Last season more than 500,000 lbs. of menthol and peppermint were exported, the largest buyer being England, the second the United States, and the third Russia. The average price per pound was $2.30 for menthol crystals and 70 cents for peppermint oil. Before the war the exports amounted to 300,000 to 350,000 lbs. Germany was the largest buyer, England the second, and the United States came far down in the list. The pre-war prices were about $2 per lb. for menthol crystals and $1 for peppermint oil. The present prices of $5 and $1.50 per lb. are too high to tempt foreign customers.

PERKIN MEDAL AWARD

Before an audience which overtaxed the capacity of Rumford Hall of the Chemists' Club, New York City, the Perkin Medal for 1920 was awarded to Dr. Charles Frederick Chandler at the meeting of the American Section of the Society of Chemical Industry on Friday evening, January 16, 1920.

It was a thoroughly sympathetic audience in that many of those present counted themselves among the former students of the recipient, and all felt the inspiration of the presence of the man who, with his eighty-three years upon him, daily continues to contribute his full share of work with a light heart and a cheery word to all. The tables were turned—he who had so often as senior American president of the Society presented the medal in years past, was now honored by its bestowal, and the outburst of applause following the presentation testified to the cordial approval of the action of the Committee of Award in thus recognizing the long life of useful service which Dr Chandler has devoted to the upbuilding of our chemical industries.

In his introductory remarks, Mr. Charles E. Sholes chairman of the Section emphasized the fact that the medal was given this year, not for some one conspicuous piece of work, but for noteworthy achievements in almost every line of chemical endeavor.—[EDITOR]

CHARLES FREDERICK CHANDLER, PERKIN MEDALIST, 1920

PERSONALITIES

By M. C. Whitaker

NEW YORK, N. Y.

To attempt to tell you something new about the personal side of Dr. Chandler's career is a difficult undertaking, when speaking to people who have been his friends and associates for years. It seems, on second thought, however, in view of my twenty-one years of intimate acquaintance with him that I might be able to recall a few instances to illustrate prominent characteristics and record the impressions which these observations have left upon my mind.

There is no man in the chemical profession who owes more to Dr. Chandler than I do, but it would be useless for me to attempt to express my gratitude in such English as I might command, and it would be out of place at this, his Perkin Medal meeting.

About thirty years ago as a student in a small western university, I became interested in the subject of industrial chemistry, and its correlated branches. I soon found that the national authority on this subject was C. F. Chandler, of Columbia. He probably does not realize that the reputation he enjoys extends far beyond the zone of his activities in New York, and reaches to every student in every school where applied chemistry is taught. Every mine and smelter which supports an assayer acknowledges its debt of gratitude to Chandler for the creation of one of the cleverest devices of that art, namely, the assay ton system of weights. It has saved millions of investments by eliminating bad arithmetic.

I little dreamed in those days that I might some time have an opportunity to know this leader of the profession which I sought to break into. In my wildest flights of imagination I did not picture myself as a student, an assistant, a confidant and an intimate friend of this great man.

You may appreciate my surprise, therefore, when, a few years later, Chandler appointed me "unsight and unseen" an instructor in the Department of Chemistry at Columbia. The reason for this selection has never been understood by me, and it has never been explained by Chandler, because it is one of those unexplainable accidents. In any event, it was arranged that I should come to Columbia and assume the duties of an assistant in the great department of which he was chief. It was further agreed that he would require the University to force upon me a salary of $83.33 per month. Salary was an extremely important consideration to me, because it was to be the first money I had ever received as a chemist, and, besides, in the absence of any other form of endowment, it was necessary to my sustenance. I was a little embarrassed by the fact that the University did not fully appreciate my position in the matter of sustenance and arbitrarily decided that the sum mentioned in the agreement should be paid, not in monthly instalments, but quarterly. However, I managed to establish the necessary credits with my landlady, and to pull through until the first quarterly check arrived.

In the meantime I was extremely busy with the work at the University. Between assisting at lectures, conducting quizzes, supervising laboratory work, correcting examination books, and interviewing students, I found time to become better and better acquainted with Chandler. By cutting out a few meals and some sleep, I was able to assist him in handling much of his burdensome detail work. During the year he suggested that I might use my vacations, holidays and such spare time as I might have by serving as his private assistant. The opportunity seemed to me the most wonderful I had ever had. Nothing was said about salary, and I thought of nothing but doing his work and getting the benefit of his experience and advice. After a few months, Chandler reminded me that I had not been paid for my work as private assistant, and handed me a check which was so big it embarrassed me, and which I could not help but feel was a great deal more than I was worth. The privilege of knowing and working with Chandler and being associated with his problems was worth more than money to me, and was all I had expected to receive.

During those early years I had an opportunity from time to time to see something of the human side of my distinguished chief. Tact is one of his greatest attributes.

It used to be, and probably still is, a source of great amusement to the students in the upper laboratories of Columbia, to drop paper bags filled with water on the heads of pedestrians. Now and then, when marksmanship is good, they hit a Fifth Avenue bus.

On one occasion, the victims were two handsomely gowned, unusually dignified, middle-aged ladies of evident social position. They swung into the Havemeyer Building, almost immediately after the accident, fairly sputtering with indignation and rage, and were met at the door by the ever-ready Chandler. They were somewhat disarmed by his genial smile, glistening eye and ready wit, and accepted his invitation to his office to discuss ways and means of properly punishing wayward students. Tea was served with liberal proportions of a flavoring extract made in New England, but named after what is destined to be a famous West Indian Island. Negotiations leading to the punishment of the students soon began to take a more hopeful trend, and in the course of half an hour the two ladies left the building, much improved in spirits, with their anger and rage replaced by smiling countenances and very audible laughter.

Chandler's earnings from his profession probably far exceed those of any other chemist in America. His generosity to others, however, keeps pace with his earnings. No one knows, not even Chandler himself, of the great financial assistance which he has given to many students. A few years ago an old Columbia graduate, unknown to most of us, died in the far west, and provided in his will that the money loaned him by Chandler from time to time should constitute the first claim upon his estate. It was with a great deal of difficulty, and without much assistance from Chandler, that we were able to determine how much money was involved. It turned out to be several thousand dollars in loans scattered over many years.

There are doubtless many cases of this kind, because during the forty-six years that Chandler was Dean of the School of Mines, he was the friend, confidant and father confessor of every one of that great army of students whose troubles are innumerable. It is out of the question for a man of Chandler's tender heart to refuse needed aid to a student. In proportion to his wealth, he gives away more than any American millionaire. His money is not spent on automobiles, yachts, fine wines, or lobster palaces, but is spent on others.

A few months ago I was invited to attend the private exhibition of the household effects of a late citizen of New York, chiefly known for his diamonds. As I stood in the center of a special room, gazing at the wonderful collection of necklaces, bracelets, handbags, slippers, garters, and stockings, I was suddenly struck with an idea. I thought of the Chandler Museum at Columbia, and recalled the innumerable times when Chandler would rush up to the University and disgorge from his pockets the most mysterious collection of teacups to illustrate some particular kind of porcelain, saucers typifying a style of decoration, vases of Wedgwood, decanters showing particular design of cutting or etching, wine glasses with special features, napkin rings, and even spoons. I wondered if there was anything in common between Chandler and "Diamond Jim," and then my thoughts turned to what a place must have looked like after a *joint raid* by these two collectors.

I have touched briefly upon Chandler's intuition, his ability to inspire others, his good-fellowship, his tact, his good-will towards others, and his hobbies. It seems to me that all of these qualities go to make up a great case for the human side of Chandler's character. I believe that we should write in large letters, and place high in the list of his distinguished achievements. and in words which I must leave to others to coin, something to express the human side of Chandler.

PRESENTATION ADDRESS

By Marston Taylor Bogert

Columbia University, New York, N. Y.

The accomplishments of sixty years of tireless, skillfully directed activity cannot be reviewed in the brief time at my disposal this evening in more than a hasty, imperfect, and superficial way, and I know that my colleagues fully appreciate the magnitude of the task assigned me and the impossibility of telling Dr. Chandler in any one evening all that we would like to say in eulogy of his many notable contributions to civilization and in expression of our affection for him personally:

> A day for toil,
> An hour for sport,
> But for a friend, life's all too short.

ANCESTRY, BOYHOOD, AND TRAINING

The first Chandlers to arrive in this country were William Chandler and Annis, his wife, who came to Roxbury, Mass., from England in 1637; but it was in Lancaster, Mass., in the house of his grandfather, Nathaniel Chandler, who graduated from Harvard in 1792, that Charles Frederick was born, December 6, 1836.

His father, Charles Chandler, was a merchant in New Bedford, Mass., where the family home was located at the corner of Third and Bush Streets, and there Charles passed his early life, in company with his sisters, Catherine and Mary, and his brother, William H., later Professor of Chemistry at Lehigh University.

His maternal grandfather was John Whitney, an old Boston merchant, and his grandmother was a daughter of John Slack On the paternal side, the Chandler ancestors were prominent in Massachusetts life, three successive John Chandlers having been Judges of Probate in Worcester County and Colonels in the Provincial Army. The Revolution broke out during the life of the last of these three, who begged to be permitted to remain neutral, as he certainly could not bear arms against his fellow-countrymen nor could he bring himself to fight against the flag under which he and his forebears had fought. But feeling ran so high that he and eight other royalists were expelled from the country and their property confiscated. This John Chandler settled in London where he lived until 1800, and where he was generally known as "the honest refugee," because he never uttered any complaint nor made any demand for reimbursement for the financial losses suffered. At his own urgent request, his wife and children had remained in America, and one of these children was the Nathaniel Chandler referred to above.

As a boy, Chandler learned much of botany and natural history in Sunday afternoon rambles with his father. At the age of 14, he attended occasional Lyceum lectures by the elder Agassiz on corals, fishes, and other zoölogical topics. The eminence of the lecturer, and the absorbingly interesting manner in which he presented his subject charmed and enthralled the budding scientist in the audience, and captivated his imagination with the splendid possibilities of such a career.

After graduating from the New Bedford High School, he continued his studies privately with a friend of the family for nearly a year, and then set out in the autumn of 1853 to secure a chemical education at Harvard, followed by study at Göttingen and Berlin from 1854 to 1856, when he received the degrees of A.M. and Ph.D. from the University of Göttingen.

AS EDUCATOR

UNION COLLEGE—In January 1857, Dr. Chandler was appointed assistant to Professor Joy at Union College, Schenectady, N. Y., and in the spring of that year they the opened chemical laboratory there, enrolling six students in the first class. In April of the same year, Professor Joy was called to Columbia College, and Dr. Chandler succeeded him at Union, lecturing to 150 seniors, most of them older than their teacher.

SCHOOL OF MINES—Upon learning that Professor Chandler was conducting commercial assays of ores for gold and silver, and also lecturing on the subject, Dr. Egleston concluded in 1864 that Chandler was the man needed to join General Vinton and himself in the project of establishing a School of Mines in New York City as part of Columbia College. A formal invitation arrived not long afterward, and Dr. Chandler signified his acceptance. To the credit of his deep sense of patriotic duty be it recorded that he delayed his departure from Schenectady until after Election Day, 1864, in order that he might not lose his vote for Abraham Lincoln.

Some vacant rooms in the basement of the old college building on Madison Avenue and 49th Street were fitted up for the laboratories and accommodation there provided for twelve students. The new school opened its doors November 15, 1864, and twenty-four students presented themselves for admission on that date. Chandler has often told in his own inimitable way how he used to open the laboratory at seven A.M., start the fire to warm it up, sweep and clean the room, and do all in his power to make the place as attractive as possible and the lot of the students a pleasant one. It was inevitable that there was passed on to these students at the same time some of his own overflowing energy and enthusiasm.

The school was a phenomenal success practically from the beginning. During the entire winter, carpenters and plumbers were kept busy installing new desks for new students and the number of students for the first year finally rose to forty-seven. During the following vacation accommodations were arranged for seventy-two students. Eighty-nine registered for the second year. Prof. J. S. Newberry was called to the chair of geology, relieving Chandler of this subject, and a complete faculty of professors and junior officers was established. A new building was erected especially for this new school, the plans of which were drawn up by Dr. Chandler himself. It was designed to accommodate one hundred and fifty students and was soon overflowing.

Although at first appointed Professor of Geology, Analytical and Applied Chemistry, and Assayer, Dr. Chandler soon was made Dean of the school and became its leading figure, all-pervading genius and chief driving force. For thirty-three years he served as Dean, and of the many able and devoted men who have built their lives into this splendid institution, none has contributed so much as he. In 1897, when the University moved to its new site upon Morningside Heights, Professor Chandler resigned his post as Dean, but continued in charge of the department of chemistry as the "Mitchell Professor of Chemistry" until his retirement from active service, July 1, 1911. In the early days he lectured upon all branches of chemistry, both theoretical and applied, but as the staff grew in numbers he transferred to his younger associates most of this so that during the later years of his professorate his lectures were mainly upon general and industrial chemistry.

It was largely through Dr. Chandler's personal solicitation and influence that the Havemeyer family generously provided the funds for the erection of a splendid chemical building at the new site. Before drawing up the plans for this building, Dr. Chandler made a special trip to Europe for the purpose of examining the construction of the leading chemical laboratories there, with the result that Havemeyer Hall, when finally completed, embodied the best that was then known in regard to laboratory construction, and was universally regarded as the finest chemical laboratory in the United States.

The Chemical Museum of Columbia University is his own creation, begun and expanded through his indefatigable labors and personal generosity and, in recognition of this fact, the trustees have very appropriately named it the Chandler Chemical Museum. For many years it was unique, and is believed to be still the most complete of its kind in the world.

Under date of January 3, 1910, Professor Chandler addressed the following communication to the president of Columbia University:

> MY DEAR DR. BUTLER:
>
> After mature deliberation I have decided that it is much better to withdraw from active service while one is in the full enjoyment of health and strength, rather than to wait until the infirmities of age make it evident to all that one has outlived his usefulness.
>
> This is my forty-sixth year of service at Columbia, and my fifty-fourth year of college teaching, and I feel that I have had my fair share of this most agreeable life.
>
> I wish to take this opportunity to express my gratitude to you and the other members of the Board of Trustees and their predecessors for the confidence with which they charged me from the outset with the various duties of instructor, dean, bursar, and registrar, and the generous support which I have always received from them.
>
> I would respectfully request that I may be relieved from the active duties of my professorship at the end of the present academic year.
>
> Very respectfully yours,
> CHARLES F. CHANDLER

The minute adopted by the trustees in accepting this resignation, after reciting briefly his career, concludes with the following:

> Professor Chandler will carry with him into his retirement the affectionate regard and esteem of two generations of students, as well as of a host of colleagues on the teaching staff of the University. The Trustees record their grateful appreciation of this long and generous career of devoted service.

He was granted a year's leave of absence on full pay, and appointed Emeritus Professor of Chemistry to take effect upon the date of his retirement, July 1, 1911.

The Columbia Alumni established a Chandler Lectureship and Chandler Medal at Columbia, and gave a huge banquet in his honor. On that occasion, President Butler spoke with deep feeling of Dr. Chandler's approaching retirement and paid a glowing tribute to the man and his work, as follows:

> In the University, as in the nation, we mark most of all, and we cherish beyond all else, the coming and passing of personalities. No substitute has been found in specialized scholarship or in technical skill or in acquired art for those precious qualities of mind and heart that make a man a great teacher to generations of students. * * * It is by the coming and the passing of the services of these personalities that we mark the real history of Columbia, and we shall be poor indeed, no matter how magnificent our site, how splendid and how numerous our buildings, how large our endowments and how great our enrollment, we shall be poor and wretched indeed when personalities—great human personalities—are no longer found in Columbia's life * * * The world is full of chemists, but there are not very many Chandlers. * * * I know that we cannot get on without personality, and I mark with sadness and sorrow the retirement from active service of a personality which has been familiar to me for thirty-two years and which has always been full of charm, abounding in loyalty, generous in doing for Columbia and the public, and anxious to find new ways in which to serve. I call that a great academic and a great human service and am glad to have had this personality on the proud rolls of Columbia.

President Butler's Annual Report of November 7, 1910, contains the following additional reference to Dr. Chandler:

> To his teaching power as well as to his effective and conscientious service as administrator, the Department of Chemistry and the School of Mines, to which it primarily belonged, owed almost everything for many years. Professor Chandler has long been a point of contact between the University and the public, between science and industry and the public health. His career is unique of its kind, and we shall not soon look upon his like again.

In commenting upon the same subject, the *Columbia Jester*, a student publication, in its issue of January 20, 1910, has this to say as indicative of the students' attitude:

> Year after year he has taken the entering classes by the hand and has led them through a course of Chemistry, Ethics and Humor, so cleverly combined that it has made men of them. It is a striking tribute to his popularity that the class never fails to stamp their applause when he enters the room. It is a striking tribute to his splendid, practical ideas of health and to his wholesome, hearty, jovial nature that he is still only a boy, and with a mind and body sound enough to do all that a boy can do. * * * We, who have had the last chance to see him and hear him in the midst of the labors which were truly play to him, should be both proud and happy that this opportunity has not been missed. Truly do we fear for the future Freshmen who will not have him as a guiding spirit. And though we lament that so intimate and cherished a connection is finally to be severed, we rejoice that our last picture of him is one of a man hale and hearty, in the full possession of all his faculties and talents, working up to the last moment at his life's profession, and yielding finally to younger hands so that he may spend his remaining years as overseer of the work he carried to so high a development.

N. Y. COLLEGE OF PHARMACY—Professor Chandler's educational activities were by no means limited to the Columbia School of Mines. Another New York institution which owes largely to him its present proud position is the N. Y. College of Pharmacy.

During its early years, it had led a rather precarious existence, and in 1866, Prof. Peter W. Bedford, of its faculty, sought Dr. Chandler's assistance in the development of its work. It is typical of the man that, in determining upon his answer, the only question he asked himself was whether or not it was to the interest of the community that he undertake it. It did not occur to him to inquire, "What is there in it for me?" He said to himself, to quote his own words, "We must have apothecaries; we can't live without them, and they must be educated, for our lives are in their hands." He therefore accepted the invitation and lectured three evenings a week throughout the winter, year after year, until some of these lectures could be transferred to new members of the staff. At first he received $400, and provided apparatus and lecture material himself. The faculty then was composed of Professors Mayer, Bedford, and Chandler.

By 1878 the College had outgrown its one room in New York University, so it purchased and remodeled the old Morton Memorial Church at 209–211 East 23rd Street. In these more commodious quarters the College grew so rapidly that in 1892 it purchased the plot at 115–119 West 68th Street and erected thereon the fine modern fire-proof structure which still stands as an enduring monument to the untiring zealous efforts of Dr. Chandler and his associates, trustees and faculty, and to the loyal support of the druggists of this city. For many years Dr. Chandler served not only as a member of the faculty, but also as vice president and finally as president, which latter position he was occupying when he received a letter from President Butler, in 1905, inviting the College of Pharmacy to become affiliated with Columbia University. This invitation was accepted by the College, and it has since been the School of Pharmacy of Columbia University. Thus was justified the faith of those who in the days of small things labored so faithfully and self-sacrificingly.

That work of this kind is not without rewards which far transcend any financial remuneration is strikingly illustrated by the remarks of Dr. Chandler at a banquet tendered him by the officers, trustees, faculty, and alumni of the College upon his retirement from active duty in 1910:

> Wherever I see the green and red lights of the apothecary in New York, there I know I have a friend. I never go into a drug store but that some one comes up and tells me he was of the class of such and such a date, or is possibly a student still. Sometimes they are boys but newly matriculated at college. Sometimes they are old gray-haired men whose stooping shoulders and faltering footsteps make them seem older than I myself; always they are friends. This has been my highest reward, this has been my most cherished compensation. The feeling that I may have helped in the upbuilding of the institution, have aided in the formation of the characters of the rising generation of pharmacists, and that this help has brought me the friendship of my students, is a source of pride and will remain a source of pleasure so long as I live.

COLLEGE OF PHYSICIANS AND SURGEONS—Another New York educational institution in whose development Dr. Chandler was enlisted not many years after his arrival in New York, and where he served with his customary distinction and success, was the New York College of Physicians and Surgeons, which later became the School of Medicine of Columbia University.

In 1872 he was appointed Adjunct Professor of Chemistry and Medical Jurisprudence under Professor St. John, and on the death of the latter in 1876 succeeded to his chair, lecturing on physics and chemistry every afternoon from five to six o'clock. This chair he held for over twenty years, retiring in 1897.

His work there, as was the case always, was progressive and constructive, and this great school owes no small part of its present international reputation and prestige to what Dr. Chandler built into it.

AS AUTHOR AND EDITOR

As an author, Professor Chandler has a long list of publications to his credit, embodying the results of research and invention, official reports, public addresses, sanitary regulations, analyses of waters, minerals, milk, etc., a survey of which shows at once the wide range of his interests and the versatility of his genius.

As an editor, he supplied for several years an American Supplement to the monthly edition of the *Chemical News* (of England) and, in July 1870, in association with his brother, Prof. William H. Chandler, of Lehigh University, founded the *American Chemist*, and continued its publication until April 1877, when it was given up to make way for the *Journal of the American Chemical Society*. Another editorial task, and one which proved most laborious, was that of Chemical Editor for Johnson's Encyclopaedia.

AS INDUSTRIAL CHEMIST

Chandler was one of America's first great industrial chemists, and aided and enriched almost every chemical industry which this country supported during the two decades following 1866.

His services have always been in demand by those great corporations whose manufacturing processes are based upon chemistry, for he has not only a thorough knowledge of that science, but also an alert mind stored with original and valuable ideas. He has been generally acknowledged to be the highest authority in this country in the field of industrial chemistry. While other able and eminent chemists have their single specialties, Chandler has been called a specialist in all branches, and is especially expert in sugar refining, petroleum refining, the manufacture of illuminating gas, photo-mechanical processes, and calico printing. He has served as chemist for the New York Gas Company, and for the New York Steam Sugar Refining Company, as consultant for the Standard Oil Company, and for various other great business interests.

He has no rival to the title of dean of the industrial chemists of the United States. Even now, at the ripe age of 83, he is laboring daily in the offices of the Chemical Foundation, Inc., helping to prepare our country for the coming German chemical competition.

One of his first and far-reaching contributions to the progress of chemical industry was the invention of the system of assay weights, as outlined in his article entitled "A New System of Assay Weights," which appeared in the American Supplement of the *Chemical News* of August 1869. Although this system has been for years the one used by all assayers and metallurgists, it is safe to say that but few of them are aware of the fact that it was Chandler who introduced it, with the aid of Becker & Son, who manufactured the weights according to his specifications.

His observations and belief in the possibilities of the Castner Process for the production of caustic soda by electrolyzing sodium chloride in a "tipping cell" with a flowing mercury cathode were communicated to the Matheson interests and they later, acting upon his advice, purchased the American patent rights and established in this country a great electrochemical industry at Niagara Falls, N. Y.

It may be of interest also to note in passing a fact which is probably unfamiliar to many of this audience, namely, that it was due to Chandler's advice and urging that the firm of Eimer and Amend started their laboratory supply business in 1874. The founders of this firm were German apothecaries who were dissatisfied with the standard of purity of the American pharmaceutical products of that day and therefore began the importation of alkaloids, etc. Chandler urged them to extend this branch of their business and to include also the importation and manufacture of chemical apparatus. How great an assistance it has been to the cause of American chemistry to have had at hand the stores of fine chemicals and apparatus provided by this firm, it is difficult to overestimate.

So much of his time was occupied in great patent suits that but little was left for investigation. I well recall his advice, when I asked him to give me some guiding principles in serving as chemical expert in such litigation. His answer was brief and to the point: "Know your lesson; tell the truth; don't be afraid to say, 'I don't know.' "

The most famous suit in which he participated was that brought in the interest of the widow and assignees of the Rev. Hannibal Goodwin, an Episcopalian minister of Newark, N. J., and an amateur photographer, who was the first successful inventor of a flexible nitrocellulose film for the kodak camera and for moving picture negatives and positives. Goodwin's opponents kept him in the Patent Office ten years before he could get his patent, when he died. Thirteen years of most strenuous litigation were required to win against the infringer. Rather than have a court investigator examine the books to determine the proper award, the defendant settled with the plaintiffs by the payment of $5,000,000, which is believed to be the largest amount ever secured in a patent suit.

Other noteworthy suits were the first synthetic coal-tar color cases, of which there were five concerned with artificial alizarin, and others later which had to do with the Roussin patents, owned by Poirier & Co., of Paris, for the azo dyes obtained by diazotizing sulfanilic or naphthionic acid and coupling with suitable amines, amides, or phenols; but to review even briefly the many notable suits in which he has been engaged would take an entire evening, as they include subjects in almost every branch of chemical industry.

AS BUILDER OF AMERICAN CHEMICAL ORGANIZATIONS

As a builder of American chemical organizations, Dr. Chandler has played a notable rôle.

He was president of the Convention of Chemists which gathered at the grave of Dr. Joseph Priestley, Northumberland, Pa., July 31 and August 1, 1874, to celebrate the centennial of chemistry, and where the first seeds were sown of what was later to become the largest and most powerful national organization of chemists the world has ever known, and of which Chandler has been twice president and many times a director—The American Chemical Society.

The founding of this Society is described in the issue of the *American Chemist* of May 1876. After the centennial meeting in 1874, the project of establishing a chemical society was often discussed by many of the New York chemists, and it was finally decided to call a meeting for the purpose. As was to be expected, Chandler at once became the recognized leader in the movement and, under date of January 22, 1876, a self-constituted committee, of which he was the guiding genius, sent out a circular letter to all chemists in New York and vicinity inviting coöperation in the formation of a local chemical society. Emboldened by the number of favorable replies received to this communication, the same committee, on March 22, 1876, distributed a second circular letter suggesting the desirability of organizing a national instead of a local chemical society, and submitting a tentative draft of a constitution and by-laws for an American Chemical Society. So many approved the proposal that a call for an organization meeting was issued on March 27, 1876, and on April 6, 1876, this meeting was held in the rooms of the New York College of Pharmacy, with 35 chemists in attendance, and with Dr. Chandler as presiding officer, and the American Chemical Society was born.

Chandler is thus the father of the American Chemical Society. It is also just to refer to him as the father of the Chemists' Club, for, although he was not the originator of the movement which led finally to its establishment, he had always spoken in favor of such an affiliation of our New York chemists, and he was the unanimous choice for the Club's first president. Without his wise and experienced guidance, his unquenchable optimism, and his financial assistance, the Club would have had a hard struggle for existence. He has been its chief reliance through good and bad weather.

AS PUBLIC SERVANT

BOARD OF HEALTH—Unquestionably Dr. Chandler's greatest services in the utilization of science for the benefit of mankind have been in safeguarding the public health and saving human lives through improved sanitary measures.

In 1866 he was invited by the Metropolitan Board of Health to make some scientific studies of various sanitary questions affecting the health of the community. Although there was to be no pay for the service, Dr. Chandler undertook it unhesitatingly, and the commissioners were so well satisfied and so convinced of the importance of the work that at the end of the year they created the position of Chemist of the Board of Health for him, a position which he held until 1873, when he was appointed president of the Board by Mayor Havemeyer, and in 1877 reappointed by Mayor Ely, his second term expiring May 1, 1883.

Among the many important matters included within the wide sweep of his investigations were the gas nuisance, dangerous kerosene, the city water and milk supplies, adulterated liquors, poisonous cosmetics, offensive trades, the removal of the stalls around Washington, Fulton and Center markets, the abatement of the sludge acid nuisance, the regulation of slaughter houses, cattle driving, the construction of tenement houses, the introduction of a proper system of plumbing and house drainage, the establishment of the summer corps of visiting physicians, the permanent system of gratuitous vaccination, and the proper care of contagious diseases in special hospitals.

In 1866, out of every one hundred deaths in the city, 53 were of children under 5 years of age. The efforts at sanitary improvement so actively conducted under Dr. Chandler's leadership, together with the increased intelligence secured by the efforts of the sanitary authorities, the sanitary organizations, and the press, succeeded in reducing this ratio year by year until at the conclusion of Dr. Chandler's services, the 53 deaths per 100 had been brought down to 46.

This meant on the basis of the city's population at that time an annual saving of the lives of 5,000 children, without considering the reduction in the death rate of persons over 5 years of age. If the latter were also included, it is fair to estimate that at least 8,000 lives were saved to the city every year as a result of these sanitary reforms. As for each death there are 28 cases of severe sickness, the total amount of good accomplished becomes enormous.

Largely due to Dr. Chandler's activity, a State Board of Health was established of which he was made a member and chairman of its Sanitary Committee. He was always active in endeavoring to secure suitable legislation prohibiting the adulteration of foods and drugs throughout the state, and, when such laws were finally placed upon the statute books, their enforcement, as well as the regulation governing the sale of kerosene, was entrusted to him. Public analysts were appointed, samples of food, drugs and oils collected, and the necessary machinery set in motion to secure compliance with these laws throughout the state. For three years he served as chairman of this Sanitary Committee.

Upon completion of his second term as president of the Board of Health, May 1, 1883, Dr. Chandler was nominated by the Mayor for a third six-year term, but the Board of Aldermen refused to confirm the nomination, and he held over for about a year. The reason for this action by the Aldermen in failing to continue in office one who had done so much for their city is a striking illustration of the eternal fight between politics and probity, and in this particular case, to the disgrace of our city be it said, politics won.

His city and state made use of his scientific training and administrative abilities in many other ways also. For several years he was president of the State Charities Aid Association and took an active part in securing state care of the indigent insane. He served also as one of the scientific directors of the New York Botanical Garden, and chemist of the Croton Aqueduct Commission. As president of the Street Cleaning Improvement Society, he performed an effective part in bringing about the reorganization of the Street Cleaning Department.

Not only the city and state, but the nation as well, called upon Dr. Chandler for public service. Secretary of the Navy William C. Whitney selected Chandler as a member of a commission to investigate the preservation of timber, and soon thereafter the president of the National Academy of Sciences, at the request of the Secretary of the Treasury, placed him on commissions to investigate the manufacture of glucose, the denaturing of alcohol, and the waterproofing of fractional currency and bank notes.

When Chester A. Arthur was President of the United States, he named Chandler a special commissioner to study the subject of American hog products and report thereon, and in 1884 appointed him a United States delegate to the Health Exposition and the International Medical Congress at Copenhagen.

Three successive Presidents, Cleveland, McKinley, and Roosevelt, appointed him a member of the Visiting Committee of the National Observatory at Washington.

At the request of the Postmaster General, he investigated the postage stamps and refuted the stories of the newspapers that they contained poisonous constituents which made it dangerous to touch them with the tongue.

Twice, in 1880 and again in 1903, he was called upon by the Secretary of the Interior to examine the original Declaration of Independence, not from the standpoint of its justice or morality, but to advise how the faded signatures might be made more legible. Some years previously a publisher had been allowed to take a wet paper press copy of these signatures, which removed most of the ink from the parchment. All that could be suggested was to go over the signatures with India ink, but this seemed too hazardous and nothing was done.

OTHER HONORS RECEIVED

In addition to the honors already recorded, the University of Göttingen, upon the fiftieth anniversary of his Ph.D. degree, officially renewed this degree and sent him a parchment to that effect.

He received the M.D. from the University of New York in 1873, and the LL.D. from Union College the same year. In 1900, Oxford University conferred upon him its D.Sc. This was indeed a signal distinction, as the only previous recipient of this honorary degree from Oxford had been the Prince of Wales. Chandler was thus the first scientist upon whom it was conferred. In 1911, Columbia also awarded its LL.D.

He is a member of the National Academy of Sciences, of practically all the leading chemical societies both here and in Europe, and of many other scientific, learned, and philanthropic organizations.

On April 30, 1910, a huge banquet was given in his honor by the chemists of America and a bronze bust of life size was presented to Columbia University. It is an excellent likeness, and now is housed in Havemeyer Hall where all may see it and where it shows to all students what the great builder of their Chemistry Department looks like.

When the Society of Chemical Industry decided to recognize its large and influential American Section, and to draw closer the bonds uniting the two nations, it made inquiry as to whether there was any one American chemist who, by the common consent of his colleagues and in virtue of his achievements, might properly be regarded as first among our industrial chemists. There was no question that Chandler was, and had been for many years, the leading figure in this field, and he therefore received the unprecedented compliment of election to the presidency of this great international society, being its first American president, and thus joined the group of distinguished men who had held that high office previously.

CONCLUSION

In the foregoing narrative, albeit in a rather rambling and disconnected fashion, I have endeavored to give you some clearer view of what Dr. Chandler's busy life has meant to the cause of chemical education, as an industrial chemist and patent expert, as a builder of American chemical organizations, as editor, author, and investigator, and as beneficent public servant. The story is well known to the older generation of chemists, but is not so familiar to the younger ones, and it is a life history with which they all should be conversant. The picture is a very imperfect one and falls far short of doing the subject justice, as none knows better than your speaker, whose privilege it has been to work by his side for the past thirty years.

We can add but little in the way of honor to one who has been so showered already with honors of all kinds, and who is first in the hearts of so many American chemists, and yet it gives us pleasure to say to him, through the award of this medal that, in our opinion, the list of its recipients would not be complete nor would it be truly representative of our greatest accomplishments in the field of applied chemistry unless the name of Charles Frederick Chandler were also inscribed thereon.

Were Sir William Perkin himself alive, I am sure that nothing would have given him more pleasure than to have seen the Perkin Medal presented to his dear friend Chandler, for when Sir William and his family last visited our shores, the Chandler home was their home.

Perkin's contribution to applied chemistry was the founding of a great industry, which has had a most marvelous development and by which civilization has been brilliantly advanced. Chandler's greatest contributions have been in the most important chemical industry of all—the making not merely of chemists, but of men, and in applying his chemical knowledge in the service of mankind to protect the health of the community and to save human life.

Thousands of lives and an immense amount of suffering are saved annually as the direct benefit of the sanitary reforms which he initiated. Other thousands of lives have been so profoundly impressed by his noble example and inspiring altruism that the world is a better and a happier place to live in. The bounds of such an influence are far-reaching indeed and its duration outruns the lives of many generations.

No student ever attended his courses without being immediately struck with the fact that here was a man of lofty ideals and noble aims who was honestly and unwearyingly trying to be of service to his day and generation, and whose actuating impulse might not improbably have been expressed somewhat as follows:

If men can say—if they but can—
"He did his best; he played the man,
His way was straight; his soul was clean;
His failings not unkind, nor mean;
He loved his fellow men and tried
To help them"—I'll be satisfied.

I am sure that I speak not alone for myself, but also for this entire gathering and for all who know him, when I say that in our judgment he has consistently lived up to that standard throughout his long and useful life, and that he has achieved a wonderful measure of success in the sense of that word as defined by Dr. William H. Nichols, who regards it "not as the acquisition of property but the making the most of one's self."

The medal is awarded this year to Dr. Chandler because, in the opinion of the jury of award, in addition to his many valuable contributions to other branches of applied chemistry, he has made such notable advances in the great fields mentioned that he has placed the entire world in his debt and brought added prestige and dignity to the profession of which he is such a conspicuous ornament.

And now, my dear teacher, guide and friend, I cannot tell you how happy I am to be the agent selected to present this beautiful medal to you—I who have received so many favors at your hands, and who would not exchange for any amount of chemical knowledge the inspiration and encouragement derived from your example of a life worth while, and a character, like this medal, of pure gold.

May it be to you a token not only of our high appreciation of your brilliant scientific achievements, but also of our deep and abiding affection! May it bring to you and those dear to you immeasurable happiness, and may you long be spared to continue your useful work and to be the friend and guide of those setting out on life's journey!

For, after all, life is a highway,
And its milestones are the years,
And now and then there's a tollgate
Where we buy our way with tears.

It's a hard road and a rough road,
And it stretches steep and far,
But it leads at last to a haven of rest
Where peace and happiness are.

ADDRESS OF ACCEPTANCE

By Charles F. Chandler

New York, N. Y.

Mr. Chairman, Ladies, and Brother Chemists: I never was more surprised than when I was notified that the Medal Committee representing the different societies interested in the Perkin Medal had awarded it to me.

I had never really considered myself eligible, as I supposed the Medal was intended particularly for discoverers and inventors of important processes in industrial chemistry. Nevertheless, I accept it with gratitude as an expression of appreciation and affection on the part of my brother chemists.

The selection of Milton C. Whitaker and Marston T. Bogert to speak for me this evening is most gratifying. There are no two men in the chemical profession for whose attainments I have a greater respect or for whose personal qualities I have a greater affection.

After having had the pleasure of presenting this most valued token of appreciation to eleven distinguished chemists, it seems odd to stand to-night in the position of the receiver instead of the giver. It is, however, eminently appropriate that Dr. Bogert should take my place on this occasion as it falls to the lot of the available senior ex-president of the Society of Chemical Industry residing in the United States to make the presentation.

I happen to be the first to receive this honor from the Society, there never before having been a foreign president. The experiment must have been satisfactory as it was soon followed by the election of Dr. William H. Nichols, then Prof. Ira Remsen, and finally by Dr. Bogert. Drs. Nichols and Remsen are not available to-night and so the duty falls upon Dr. Bogert as the representative of the Society of Chemical Industry.

I think that there was another reason for selecting Dr. Bogert to make the presentation address. He has had experience at the banquet of the chemists, April 30, 1910, when he conspicuously demonstrated his ability to say the kindest and most flattering things about his "old professor."

Dr. Bogert has given you such a comprehensive account of my life and experiences, it is hardly necessary for me to go very deeply into the subject. I will therefore select only a few incidents which may possibly interest you.

When I was about 14 years of age and attending the New Bedford High School, the incident occurred which settled my career for life. There was a young instructor who had a class in chemistry which I attended. He made the subject so interesting that I decided that I must be a chemist. I had a little work shop which I promptly converted into a chemical laboratory, had the tinsmith make me a gas holder and amused my three or four intimate playmates by making oxygen, hydrogen, olefiant gas, and various other experiments. The impression which this teacher made upon me has lasted ever since. Two or three years ago I had occasion to give a lecture in New Bedford and I opened it by recalling my school days and I enlarged upon the influence which this young teacher had exerted upon my life. I was subsequently informed that he died while still very young. It was in 1851–52 that I attended his courses. A few days afterwards I received the most touching letter from his aged widow who is still living and had been told what I had said of her husband. Her letter brought tears into my eyes. "Nothing had given her so much consolation and happiness since his death."

In 1853 I entered the chemical laboratory of the Lawrence Scientific School and spent a year under the instruction of Prof. Eben N. Hosford, a most charming man. Here I pursued a well-arranged course of instruction in qualitative and quantitative analysis.

Here another incident occurred which had a profound influence on my subsequent life. Two strangers visited the laboratory one day and we half-dozen young chemists were introduced to them. One was Prof. Josiah D. Whitney, the eminent mining engineer and geologist who five or six years afterward became a very intimate friend of mine; the other was Dr. Charles A. Joy, who had just been appointed professor of chemistry to take charge of the new laboratory at Union College, Schenectady. Professor Joy told us that he had just returned after a course of 4 years' study in Germany in the laboratories of Friedrich Wöhler and Heinrich Rose. I subsequently wrote him for further information on the subject of studying in Germany and received a full and enthusiastic account of the advantages not only of studying in Germany but of studying with these particularly distinguished chemists. It resulted in my spending my next year in the University of Göttingen. I was fortunate in being placed at once by Professor Wöhler in the laboratory for advanced students which was under his personal direction. I took several courses of lectures and practical instruction, not only in chemistry but in physics, botany, and mineralogy. We had a large colony of Americans in Göttingen during the year, most of whom were studying chemistry and some of whom have subsequently held most important positions in the United States. As I was the youngest of them all it was a great privilege for me to enjoy the companionship which was quite intimate in that small town with such men; one of them, Professor Goodwin, was a Harvard professor of Greek; another, Professor Harkness, who was there with his wife, was professor of Greek in Brown University. At the end of the year Professor Wöhler who had been a father to me and had invited me frequently to his house, induced Prof. Heinrich Rose to take me into his private laboratory as an assistant where I spent a year working in the same room with him. He, too, was a father to me, and invited me frequently to his house. His brother, Gustave, with whom I studied mineralogy, was equally friendly. I attended several courses of lectures in general chemistry by Heinrich Rose, industrial chemistry and physics by Professor Magnus, and physics by Professor Dove. At the houses of the two Roses, I used to meet some of the most distinguished scientists in Berlin, particularly Poggendorf, and Ehrenberg, the father of microscopy. I also had the pleasure while in Berlin of spending a couple of hours with Baron Von Humbolt in the Royal Palace in Potsdam. Both Wöhler and Rose gave me the most interesting material to work upon in their laboratories, either for the purpose of preparing a constituent in some quantity or for making accurate analyses of the minerals. For example, I worked upon the following materials: Selenium, tellurium, lithia, thoria, yttria, molybdic acid, tungstic acid, cerite, columbite, tantalite, sarmaskite, and yttrotantalite, and other more common materials.

At the end of my second year in Germany I was asked to put the work that I had performed in the laboratories of Wöhler and Rose into the form of a dissertation, which I did. It was accepted and printed in Göttingen at the University Press in 1856 and I received without examination, in consequence, my degrees of A.M. and Ph.D., or as they call it in Germany, Dr. Phil.

On my return to America late in the summer of 1856, I found an invitation awaiting me from Professor Joy to come to Union College and accept the position of assistant in the laboratory. This invitation I promptly accepted and on the 9th of January, 1857, I began my professional life. I felt under such obligations to Professor Joy for having directed me to Europe that I did everything I could in the laboratory for his convenience and comfort. In four months he was called to Columbia College and left at once to take the position. Fortunately for me, the venerable president of Union College, the Reverend Eliphalet Nott, had so much confidence in my abilities that he offered, if I could lecture to the senior class, to put me in charge of the chemical department and give me the title of Professor when I was old enough to merit it. I remained at Union College until the fall of 1864; was married and given a house which had formerly been occupied by President Nott; and established courses of lectures in the different branches of chemistry, including agricultural chemistry, and in mineralogy and geology. Then by a happy accident I was invited by Professor Egleston to join him and General Francis Vinton in establishing the School of Mines at Columbia College, which has proved such a great success. The most fortunate circumstance in connection with this embryo School of Mines was the fact that we had no salaries. My friends ridiculed and lamented what they considered my rashness in accepting what seemed such an unpromising appointment. But it turned out a great success. The School not only grew rapidly into a large enterprise but it gave a most powerful impetus to the growth and development of Columbia College, which, although it had been in existence for more than 100 years, had only 155 students, almost exclusively residents of New York City. This School of Mines, which quickly became a school of every variety of engineering and chemistry drew students from all over the United States, and spread the name and reputation of Columbia College everywhere, while the graduates, particularly the mining engineers, carried the name of Columbia to Australia, New Zealand, South Africa, South America and Mexico.

Starting at Columbia with no salary at all, with only the expectation of receiving one-third of the fees that might be paid by any student who might attend, we were naturally permitted to take any outside work that was congenial, which did not interfere with our duties in the School of Mines. I was soon enabled to take advantage of this privilege by giving afternoon lectures from five to six at the College of Physicians and Surgeons, and evening lectures at the College of Pharmacy, and also to accept invitations for professional work of different kinds.

One of the most promising invitations I received came to me from the Metropolitan Board of Excise. The members of this Board not being chemists were imbued with the idea that there was an enormous amount of adulterated alcoholic beverages sold in New York and as they had a very high license and a million of dollars to their credit in the bank, they started out to put a stop to this adulteration and I was invited to act as their expert to analyze the samples and to appear in the courts as their representative. When they inquired of me how much I would demand for making these analyses and appearing in court, I told them it would depend upon the number they were likely to have. They told me that there were 8000 liquor dealers and that it would certainly average three samples each, so I agreed to a fee of $20 for each case, no matter how troublesome it might be. This they considered reasonable, and when I figured it up I saw a prospective $480,000. They promptly sent me 40 samples upon which I exhausted every possible chemical test. These samples came from Mulberry Bend and other localities where the poorest liquors are probably dispensed. They consisted of brandies, whiskies, rums, and gins. Some were of very good quality, some were not so good, but not a single one contained any objectionable constituent; not one was adulterated. I must confess that I was not much surprised because I had had some previous experience in making such analyses, especially for the Vermont State Liquor Agency, and I knew that the newspaper stories of adulterated and poisonous liquors were without foundation. I received a check for $800 according to contract and never another sample for analysis, and I charged $479,200 to profit and loss.

KEROSENE INDUSTRY

In the year ending October 31, 1869, there were 98 fires caused by kerosene accidents in New York City, and 31 in Brooklyn. There were 52 persons burned to death in New York City from the same cause, mostly women and children. It was generally supposed that these accidents were due to the fact that kerosene consisted of hydrocarbons, similar to those of "camphene" and "burning fluid," which were known to be inherently dangerous and could not be made safe. Camphene was refined spirits of turpentine, and "burning fluid" a mixture of this with alcohol; both extensively used, being very much cheaper than sperm oil, which retailed at $2.00 per gallon. When this matter was called to my attention, I said at once, "Kerosene can be made safe," and took up the investigation of the subject at once.

Manufacturers of kerosene and chemists had decided that all that was necessary to make the oil safe was to separate the lighter oils, gasoline, benzine, and naphtha, and I believed that they did so. A standard of quality had been adopted by them. The kerosene oil must not evolve a combustible vapor below 100° F., and must not take fire below a temperature of 110° F. On purchasing 78 samples in shops in the city, I found that one sample was pure naphtha, while every one of the other

78 was adulterated with naphtha. Not one of them came up to the standard of the manufacturers. I had a sample of real kerosene for comparison which I obtained from the works of a friend of mine, Dawner, of Boston, which had a flash point of 109° F. and a burning point of 128°.

Just as I finished my experiments there was a terrible accident in New York in which a mother and child were burned to death. I sat up all night and wrote my report, January 11, 1869. It was manifolded at the Board of Health and given to all the papers, in which it was printed in full, and later published all over the country. The Board of Health of New Orleans had it printed as a hand bill, and left a copy at every door. It was quoted in Berlin and in Rome.

On January 21, a supplementary report was made showing the temperatures reached in 23 house lamps, of glass and of brass, of different sizes, after periods from 1 hr. to 7 hrs. After 1 hr. the highest was in a brass lamp 100° F., the lowest in a glass lamp 77° F. After 7 hrs. the highest was in the same brass lamp 91° F., the lowest in a glass lamp 78° F.

The investigations were continued and later in the year a third report was made containing the following additional results, with a new collection of samples from retail shops in New York City:

	Samples
1—Safe oils complying with requirements	21
2—Dangerous oils, flash point below 100°	280
3—Still more dangerous, flash point below 100°, burning point below 110°	306
4—Pure naphtha	29
TOTAL NUMBER OF SAMPLES	636

A fourth investigation was made and reported, March 18, 1891, of a much more elaborate character which covered 110 printed pages. This was published and Mr. Charles Pratt asked permission to print 10,000 copies, placing an advertisement on the cover of his famous extra-safe oil, known as "Pratt's Astral Oil," which flashed at 125° F. and burned at 138° F. Permission was cheerfully granted.

The Board adopted a sanitary ordinance limiting the sale of oil having a flash point below 100° or a burning point below 110°, and appointed inspectors and equipped a testing laboratory, and before long kerosene accidents became very rare, and when they did occur generally resulted from kindling the fire with kerosene or some other kind of criminal carelessness. Not long after this I was engaged, in company with Professor Silliman, to act as an expert witness in a suit brought against infringers by Downer and Company, of Boston. This company had worked on oils obtained from the destructive distillation of coal, and also on petroleum. By employing a special process they produced, among other products, two specially "high test" oils:

1—"Downer's Standard Kerosene," flash point 115°; burning point 128°.
2—"Downer's Mineral Sperm," flash point 262°; burning point 300°.

I will quote here two paragraphs from a lecture on "Combustion," which I gave before the American Institute, January 5, 1872, immediately after the great fire in Brooklyn which was so disastrous to life.

> Naphtha is not explosive; vapor of naphtha is not explosive; it is a mixture of naphtha vapor and air, in certain definite proportions, which is explosive. If, in experimenting, we do not hit the proper proportions, we fail to produce an explosion. Any oil that will emit an inflammable vapor at any temperature below 100° F. is liable to form explosive mixtures of vapor and air, and is dangerous. I know of no process by which the lighter products of petroleum, gasoline, naphtha and benzine, can be made nonexplosive or safe, nor do I believe that there is any such process. If any oil takes fire at ordinary temperatures, or below 110° F., it is proof positive that it is dangerous, and no argument or experiment can prove anything to the contrary.
>
> This coat on its iron frame is a good representation for our purposes of a victim to kerosene. I will drench him with good kerosene; you see now that though I hold a candle to him he is in no danger. I will now throw a little of Smith's "Safety Oil" upon him; you see the moment the candle is brought near him he bursts into flames. I will save the poor wretch from a painful death by bringing the Babcock Fire Extinguisher to bear upon him. I have put him out; but were he human his days would be numbered, as a painful death would be sure to follow such frightful burns as those he has suffered from Mr. Smith's safety oil. It is said, and I believe with truth, that the burning of a square foot of the human body is sure to cause death.
>
> Before leaving this portion of the subject, I want to show you how safe it is possible to make petroleum oil. I have here a pail containing three gallons of Downer's "Mineral Sperm Oil." Into it I will plunge this mass of cotton waste till it becomes saturated with the oil; now as I raise it you see it is dripping with the oil. On holding the candle to the oily mass you see I have considerable difficulty in setting it on fire, but by heating it in one spot I shall finally heat a portion to a temperature above 300° F.—its burning point—when it will take fire. Now you see I have succeeded in starting combustion, and the burning oil quickly heats the rest of the mass till we have now a flame ten or fifteen feet high. You need not feel alarmed, for I have the flames entirely under my control. I will now plunge the burning mass into the pail of oil; you see it is at once extinguished. The "Mineral Sperm" is actually a fire extinguisher.
>
> But this oil will stand a much more severe test. Here we have a large pan of oil on a water bath. These two large alcohol lamps have raised the water to boiling; you see the steam escaping from this vent; the oil is at 212° F., 112° above the standard flashing point and at 102° above the standard burning point of safe oil. Yet you now see that this mass of cotton waste which was saturated with the oil, and was but a moment ago wrapped in flames, is now quietly extinguished. The "Mineral Sperm" is a fire extinguisher even when heated to 212° F. Am I wrong in saying it is practically as safe as whale oil?

The Standard Oil Company, then recently organized, manifested a great interest in my work on kerosene, and employed me as an expert in law suits, brought against them by persons who erroneously believed them using their patents, generally worthless, without their consent.

OHIO OIL—Some years later, when what was known as "Ohio Oil" was obtained in Ohio, Indiana, and Illinois, in considerable quantities, the company received word from their German associates that the German government had been informed by their rivals that while the Standard Oil Company was supplying the American market with the superfine Pennsylvania oil, it was sending to Germany the poor, offensive Ohio oil. In consequence, the Imperial government was about to permanently forbid the importation of this Ohio oil into Germany. A high officer of the Standard Oil Company came to me and begged me to go at once to Germany and convince the German government that the Ohio oil which his company exported was first purified by the process invented by Herman Frasch. This was one of the inventions for which your committee, a few years ago, awarded to Frasch the Perkin Medal.

President Low granted me leave of absence, and I immediately visited the great works erected at Whiting, Indiana, for the special treatment of Ohio oil by the Frasch process. The impurities which had rendered the oil and all its products so offensive were certain compounds of sulfur, of which element the oil contained about one per cent. Frasch's process consisted in first dividing the crude oil by distillation into three fractions:

1—Lighter constituents—gasoline, naphtha and benzine.
2—Medium oil for lamps.
3—Heavy oil for lubricating, and paraffin.

These three fractions were then entirely freed from the sulfur compounds by distillation in huge stills, while mixed with large quantities of oxide of copper, with constant stirring. The effect was magical. Not a trace of the offensive odor was retained by either of the products.

I met at the Whiting works the chemist in charge, Dr. William M. Burton, a Heidelberg graduate. He showed me everything and answered every question. When I told him that I was going to Berlin to explain the situation, a longing look overspread his face, and he remarked that he had not been in Germany since he graduated. I caught the look and asked him if he would like to go with me. He replied that he would give anything to go. I found no difficulty in persuading the company to give him leave of absence, and so I had a most agreeable and useful companion.

Before I sailed I also visited the works at Olean, N. Y., at Philadelphia, and at Brooklyn. So there was nothing in the treatment of petroleum that was not imparted to me. We went off together. It seemed wise, before we called upon the representatives of the government, to visit and satisfy the men who would be most likely to be consulted by them. So after visiting the representatives of the Standard Oil Company, in either Bremen or Hamburg, I have forgotten which, we went to Carlsruhe and explained the whole matter to Dr. Engler, the German expert on petroleum, giving him samples of the Ohio kerosene, and explaining how he could prove the absence of sulfur, if the entire freedom from offensive smell did not satisfy him.

Then we went to Zurich and explained the matter to Dr. Lunge, the distinguished industrial chemist. On arriving in Berlin, we adopted the same tactics with the Imperial Health Department, with the same success. With all these parties I had enjoyed an acquaintance for some years, so we were cordially received and our statements readily accepted. An hour spent with Count Posidowski, the Imperial Minister of the Interior, settled the business.

A few years later I was sent to Germany to attempt to prevent the threatened establishment of an extra high standard for all imported oils to be considerably above 100° flash and 110° burning. This time I did not have the company of Dr. Burton. As before, I first went to Carlsruhe to argue the matter with Dr. Engler, but to my discomfort I found that he was in the Austrian Tyrol, near the glaciers. There was nothing to be done but to follow him, so I crossed Lake Constance and took the train for Vienna, leaving it the next morning at Bludence. Here I hired a man to drive me to my destination, which was a day's journey. At noon we stopped at a cross-road village for lunch and to change horses. After eating my simple lunch of "Butter brod" and "Schweizerkäse," and drinking my "Beyrich," I started out to see if there was anything interesting in the village. Strolling into the country store I inquired of the proprietor in German "if he sold petroleum." He replied, "Yes, indeed." I inquired what kind and he said, "Amerikanisches." "Is it not much more expensive than that from the neighboring wells in Roumania and Galicia?" "It is indeed," he replied, "but it is so much purer; it will burn in any lamp without smoking, while the other oils will burn only in a special lamp." He assured me that the peasants willingly paid the extra price. This interview gave me my trump card. Engler saw the point at once, and so did the Imperial Board of Health at Berlin, and so did Count Posidowski. I made it clear to them that if they raised materially the standard of oil to be permitted to enter Germany, the only result would be that the Standard Oil Company would get 50 gallons of such oil out of 100 crude, while they were getting 60 at that time. It would have no real advantage, while the German people would be obliged to pay as much for the 50 gallons as they were paying for the 60 gallons. He saw the point and that was the end of it.

Some years later a bill was introduced in Parliament to accomplish the same result in order to help the Scotch manufacturers who made a comparatively small amount of kerosene from the Bog Head mineral. I was in Paris at the time and, in response to a telegram from the Standard Company, I went before a Parliamentary Committee and made the same argument. A member from the Bog Head district, who was working for the bill, had before him a copy of my last report of 1871, and identified me as the author, and then asked me if I had not intimated therein that "the higher the flash point, the safer the oil." I replied that I had, but at that time we had not had as much experience as at present. Time had shown that "100° flash" was sufficient to insure safety, and that that grade of oil was generally used in the United States and exported all over the world, and that lamp accidents were very rare.

Further I reminded him of an English nobleman who lost his life by the explosion of an extra-high test oil, because the oil evolved just enough vapor to make an explosive mixture with the air in the lamp, while the 100° flash evolved enough vapor to render the air in the lamp nonexplosive.

Several distinguished English chemists, Sir Henry Roscoe, Sir Boverton Redwood, and others gave similar testimony and the bill never passed the committee.

In 1867 Dr. Elisha Harris, of the Metropolitan Health Department of New York, came to see me and told me that the Commissioners were not chemists and did not realize how much chemistry had to do with the public health and did not care to devote any portion of their income to this subject. He asked me if I would be willing to do some work for the Department without charge. I promptly accepted his invitation and interested myself at once in a great variety of subjects, most of which I shall have to omit discussing.

WATER INVESTIGATIONS

CROTON WATER—There are two or three matters, however, which interested me very much, one of these was water. I began analyzing the Croton and Ridgewood waters every week during the three or four summer months, and I continued for several years, either myself, or, when I became president of the Health Department through Professor Waller, to keep informed with regard to the water supply of these two cities. I found that these waters were then and have been ever since among the purest waters supplied to any cities in the world. I do not believe that a case of sickness was ever caused by either one of them. General Green, who was at one time the engineer of the Croton aqueduct, was so interested in my work that he had me appointed consulting chemist for the department, and took me all over the Croton watershed that I might become familiar with the sources of the water. It is a source of constant regret to me that ill-informed persons, even physicians, are so ignorant on this subject that they advise families not to use the Croton water for drinking purposes unless it has been filtered or boiled, or both, and the result is that millions of dollars are spent in New York every year for bottled waters; not only in families who can ill afford the expense, but in down-town business offices. During the 56 years that I have lived in New York, I have used the Croton water in my family without filtering or boiling, and never has anything occurred to lead me to suppose that it was not perfectly satisfactory and wholesome.

BOILER WATERS—Another phase of the water question occupied my attention for a year when at the request of the New York Central Railroad Company I studied the subject of boiler corrosion in locomotives, boiler incrustations and feed water. I began this work at Union College and completed it in the School of Mines, publishing my results. I analyzed numerous specimens of incrustations, finding that some of them consisted of carbonate of lime; others of a mixture of carbonates of lime and magnesia; others of sulfate of lime. I also investigated the different brands of boiler medicines, most of which were frauds, and the one which seemed to be an excellent one was sold to the railroad for five times what it cost to make it, and the engineers couldn't bring their trains in on time unless this particular medicine was supplied by a particular firm. In the end, I analyzed all the feed waters employed on the road between Albany, Buffalo, and Niagara Falls, classified them as to quality, indicating those that were too bad ever to be used and causing the water stations to be abandoned, and directing the best choice to be made among the others.

HUDSON RIVER WATER—In 1871 I was called upon by the Water Commissioner of Albany to investigate the waters of the

Hudson River, to ascertain whether it would be safe to take the water above Albany and below Troy to supply the city as they had found it almost impossible to procure an adequate source of supply within reasonable distance and at such a cost as the city could afford to pay. I took up this investigation with great doubts of the fitness of this water for the city supply. I made the most careful investigations and analyses and was surprised to find that there was no reason why this water could not be used in the city of Albany. I sent in my report in 1872, stating my conclusions, with a special discussion of the destruction of the sewage contamination of large rivers caused by dissolved oxygen. I had obtained a great deal of information on this subject from the annual reports of the British Water Commissioners. The report was published and indignation meetings were held in Albany and no end of abuse was poured upon my head. The Water Commissioners were very sensible men, however; they said, "there is no sense in abusing Chandler, disprove his facts, meet his arguments, or keep quiet." My facts could not be disproved and my arguments could not be met, and consequently the Water Commissioners put up the pumping station, supplied the water to Albany, and in a short time the Health Officer of Albany informed me that the water was entirely wholesome and satisfactory.

In 1885 it became necessary to increase considerably the pumping facilities above Albany, and the Water Commissioners wrote me, calling attention to the fact that, since I made my first investigation and report in 1872, bacteria had become fashionable and were now supposed to be terrible creatures capable of producing all kinds of diseases, and whether I cared to revise the opinion which I gave them 13 years before. It happened that I was quite familiar with what had been published with regard to bacteria, having quite a library on the subject, and having had occasion to make myself specially familiar with them in order to prepare an article on fermentation for Johnson's Encyclopaedia about 1874, so I wrote the second report on the waters of the Hudson River, which was published in Albany in 1885, containing a discussion of possible bacterial contamination of water; it was not to be feared.

Fourteen years ago while in Europe I was cabled to look up the ozone treatment of city waters. Accordingly, I visited Berlin, Paderborn, and Paris, where experiments had been carried on. At Paderborn the process was in full operation, although the water supply was entirely above suspicion. The water descended slowly through a wide cylinder, while the ozonized air bubbled up through it. The effect was marvelous. The ozone seemed to destroy the organic matter, which, though minute, was sufficient to conceal the true color of the water, for when the treated water poured into a large snow-white vat it was very distinctly blue.

SARATOGA WATERS—In the early years of my residence at Union College I became interested in the Saratoga waters. I found a great diversity of opinion as to the nature of these waters, some local physicians telling their patients that there was such a great difference in the waters that it was not safe for them to drink them except after the physician had carefully diagnosed their cases, had directed them as to which waters they should imbibe, what quantities of each, and at what times of day. The owners of the Star Spring employed me to make a careful analysis of their water and soon it became the fashion to have the waters analyzed by me. As the waters contain a great variety of constituents, including small quantities of iodine, bromine, baryta, lithia, etc., I had to charge a good, round figure, which those who could afford it cheerfully paid; and as I was extremely anxious to analyze all the waters, for those who could not afford to pay my fee, I made the analyses gratuitously. Including springs and artesian wells, I analyzed about a dozen different springs in Saratoga and three at Balston. Instead of the waters differing from each other, I found that they all contained the same constituents, counting out one or two sulfur waters in out-of-the-way places which I never took the trouble to analyze. The total amount of solids varied from a minimum of 302 grains in one U. S. gallon to 1,184 grains, the latter being the amount in the Balston artesian lithia well, which was bored over 600 ft. deep. There is an interesting story about the Highrock Spring at Saratoga. It is the oldest known spring there and it consists of a volcano-shaped rock about 4 ft. above the level of the surrounding ground with a hole or crater in the center supposed at that time to be of almost unknown depth. This hole had a diameter at the top or mouth of 8 or 10 in. and the water rose to within about a foot of the top. Saratoga was first visited by a white man when Sir William Johnson went there in 1767. He was told by the Indians that according to their traditions the water formerly rose and overflowed regularly and continuously, but not within their recollection. This must evidently have been the case, for the Highrock is composed of tufa, carbonate of lime, and contains the impressions of leaves and the shells of snails here and there. It had evidently been formed gradually by a deposition of carbonate of lime from the water, which is a common occurrence with this class of waters. After a time, during my association with Saratoga, this spring changed hands and the enterprising purchaser decided to make the water resume its old habit of overflowing the rock. In order to do this he had oblique holes drilled on different sides around the edges of the rock toward the center. He then introduced wedges and succeeded in detaching the rock from its base. He then put chains underneath and hoisted it off one side. Then they enlarged the hole up through which the water came and went down expecting to find some leak which had prevented the water from rising any higher, and which they intended to close. They found beneath the high rock a layer of tufa 7 ft. thick, including some muck, below that they found 2 ft. of tufa clean, below that one foot of muck and below that again 3 ft. of tufa. Just below the rock itself they found 4 well-preserved logs put crosswise at right angles to make a curb for the spring which must have been placed there before the Highrock was formed, and, finally, at a depth of 17 ft. they found a considerable quantity of half-burned embers and charcoal, showing that visitors had made fires before that 17 ft. of material had been deposited.

An enterprising citizen of Saratoga was very anxious to ascertain when those fires had been made and remembering that the botanist ascertained the age of a tree by making a cross section of the stem and counting the lines or rings from the center to the circumference ascertained the number of years it had been growing, he took a piece of the Highrock, smoothed it against a grindstone, and found it showed 81 lines to the inch, so he said it must have taken 3,840 years to form. He continued his calculations for the remaining 13 ft. The following table shows his figuring:

THE HIGHROCK

		Years
The Highrock	4 ft.—81 lines to inch.........	3,840
Muck and Tufa	7 ft........................	400
Tufa	2 ft.—25 lines to inch.........	600
Muck	1 ft........................	130
Tufa	3 ft........................	900
	TOTAL................	5,870

According to his education the world had existed only

4,004 yrs. before the Christian Era
1,870 yrs. after the Christian Era

5,874 yrs. in all
5,870 yrs. since the fire was made

4 yrs. after the Creation

Consequently, there was no one living on the face of the earth excepting Adam, and he was 4 yrs. old. I hope you will pardon my frivolity in presenting this ridiculous proposition to you, but it went the rounds in Saratoga.

There is one other interesting matter connected with the Saratoga Springs. Some years ago a sanitarium near the Hawthorn Spring set up a pump and drew large quantities of water from a tube of some depth, with the result that the Hawthorn well was very seriously affected.

A law suit resulted in which my testimony and that of others was taken in favor of Hawthorn, with the result that the sanitarium was enjoined. At or about the same time, a company began to bore numerous wells some little distance from the Springs, introduce steam pumps, commercialize the carbonic acid gas, and permit the water to run to waste. In a short time the springs began to show the disastrous effects. The waters no longer spouted from the spouting springs, the others no longer came to the surface, and pumping had to be resorted to. In addition to this the diminished pressure of water in the springs permitted fresh water to permeate into them and dilute them.

Again I was called as an expert, and testified to the ruinous effects of this pumping. The company produced experts who declared that it was absolutely impossible for this pumping to have any effect whatever on the springs, and that the falling off of the springs must be due to natural causes. The judge, however, was a second Solomon. He directed the defendants to stop pumping for 48 hrs. to decide the question, and ordered the sheriff to see that the order was obeyed. Within 24 hrs. the whole town gathered around the Hawthorn Spring to see the water again rising, brilliant in the sun with gas bubbles, and overflowing the large glass cylinder placed over the spring. In the end the State bought all the springs and wells and established a State Reservation.

LEAD IN DRINKING WATER—The question of lead in drinking water came to my attention at an early day. Physicians reported cases of lead poisoning. I will mention as a single example an elderly gentleman's case which was diagnosed as lead poisoning. No probable source of the lead could be suggested till the doctor interviewed the cook, and learned that her first duty in the morning was to place the old gentleman's "wheaten grits" cereal in a bowl, draw water upon it, and after a while boil it. This fact suggested lead in the water. My attention was called to the subject and I found that water which had stood all night in the pipe of my own house contained a little lead, which might, as lead is a cumulative poison, ultimately produce serious results, if such water were often used. Looking further into the matter, I found that owing to the low pressure in the water pipes a great many houses were provided with pumps and tanks to supply the upper stories. Examination of the tanks developed the fact that they were usually lined with lead, and the water thus became contaminated.

Examinations were also made of Croton water, which had been in contact with lead for different lengths of time, under commonly occurring circumstances, of which the following are the results:

1—A gallon of Croton water from a lead-lined cistern, in which it had stood several weeks, was found to contain 0.06 grain of metallic lead.

2—A gallon of water which had remained 6 hrs. in the lead pipes of my residence yielded 0.11 grain metallic lead, a considerable portion of which was visible to the eye, in the form of minute white spangles of the hydrated oxycarbonate $(PbO_3.H_2O + PbO\,CO_2)$.

3—Water drawn from one of the hydrants of the School of Mines laboratory, in the middle of the day, when the water was in constant motion, yielded traces of lead. This water reached the school through about 100 to 150 ft. of lead pipe.

The following paragraphs are quoted from a lecture delivered before the American Institute in the Academy of Music January 20, 1871:

> These results indicate the source of many hitherto unaccountable cases of lead poisoning, and are of a character to alarm the residents of New York, and lead them to adopt precautionary measures for protection against this insidious cause of disease.
>
> A celebrated case occurred in the royal family of France, at Claremont, where one-third of the persons who drank of the water were affected. This water contained only one-tenth of a grain of lead in a gallon. As little as 1-100 grain of lead to the gallon has been known to produce palsy in persons who habitually drank it. It is a great pity that the peculiar advantage of lead as a material for the manufacture of water pipes is more than counterbalanced by the danger of lead poisoning

This subject attracted a great deal of attention at that time. The Board of Health put an end to the use of lead-lined tanks and the public was warned against drinking water that had stood long in the pipes. About this time tin-lined lead pipe was invented. It was made by casting lead around a hollow cylinder of tin, and then drawing the mass down to a pipe of the desired size. I found that the heat of the melted lead was liable to soften the tin lining to such a degree as to alloy it with the tin even clear to the inner surface of the tube. A suggestion of mine overcame this difficulty. A separate hollow cylinder of tin was placed in a surrounding cylinder of lead of such size as to leave nearly a quarter of an inch of space between the two. Then melted solder was poured between the two cylinders; they were perfectly united without melting the tin perceptibly, and a perfect tin-lined pipe was produced. I used this pipe throughout my country house at West Hampton, and one of the spring companies at Saratoga employed it for a deep spring, using a very large sized pipe, 2 in. or more. A test of the proper condition of the pipe was easily made by cutting off a section about an inch long, holding it in forceps, and carefully heating it over a Bunsen burner. If it was in good shape the solder would first melt, as could be seen by the eye, and the tin tube could be shaken out in a sound condition. If, on the contrary, the lead had alloyed the tin the entire lining sloughed off on heating. Special joints were devised and the invention was a complete success. But the cost of plumbing was considerably increased, both for material and labor, and the invention never came into general use.

POISONOUS COSMETICS

Before I leave the subject of lead poisoning I must say a word with regard to the poisonous cosmetics which I examined in 1869. Hair tonics, washes, and restoratives were much advertised and sold. The following are the results of my examinations of those sold in New York City. Only one was free from lead, that was Hoyt's Hiawatha Hair Restorer, which was an ammoniacal solution of nitrate of silver, and harmless. Here are the others:

GRAINS OF LEAD IN ONE FLUID OUNCE

Clark's Distilled Restorative for the Hair	0.11
Chevalier's Life for the Hair	1.02
Circassian Hair Rejuvenator	2.71
Ayer's Hair Vigor	2.89
Prof. Wood's Hair Restorative	3.08
O Brien s Hair Restorer America	3.28
Gray's Celebrated Hair Restorative	3.39
Phalon's Vitalia	4.69
Ring's Vegetable Ambrosia	5.00
Mrs. S. A Allen's World's Hair Restorer	5.57
L. Knittel's Indian Hair Tonique	6.29
Hall s Vegetable Sicilian Hair Renewer	7.13
Dr. Tebbett's Physiological Hair Regenerator	7.44
Martha Washington Hair Restorative	9.80
Singer s Hair Restorative	16.39

These fluids consist of an aqueous solution of acetate of lead, generally containing a sediment of flowers of sulfur. They are to be well shaken before use and when applied at intervals to the hair are said to "gradually restore the original youthful beauty and color." Six lotions or washes for the complexion were examined, one contained corrosive sublimate and sulfate of zinc. Seven enamels for the skin were examined. Three contained oxide of zinc, and three others carbonate of lead.

THE PLUMBING SYSTEM

I should have been very glad to have had time to explain the improved system of plumbing which resulted from the experimental set of plumbing arrangements which I erected at the Board of Health building, where with a kitchen sink, butler's pantry sink above it, a wash bowl above that, and a bath tub above that, all with glass traps for ready observation, it was easy to demonstrate the absolutely unsafe condition of the plumbing, not only in New York, but everywhere else in this country.

The result of this was an improvement resulting in carrying the soil pipe through the roof, of undiminished caliber; the back-airing of all traps by means of a separate pipe running through the roof; the running trap between the house and the street sewer; and the inlet for fresh air between the house and this trap. This system was approved by the plumbers and fixed by law, and was placed under the control of the Board of Health. It was generally adopted throughout the country, and there was no more talk about sewer gas as a cause of disease. Microbes took its place. Patent traps were not accepted as substitutes for good old-fashioned S-traps. By the way, I have just learned from Mr. A. E. Hansen, hydraulic and sanitary engineer, who is advisor to the Master Plumbers' Association, that an effort is now being made to force the plumbers to adopt a "patent trap." To pass such a regulation would be a crime against the inhabitants of this city.

CONCLUSION

There are many other topics to which I would delight to call your attention such as:

My connection with the first production of oleomargarine, that cheap, wholesome article of food which has been so handicapped by the Government; the introduction of cheap water gas in New York and in Boston, and the sustaining of the Lowe process for its manufacture; my study of sugar refining in Europe in 1869; and the Hunters Point nuisance.

I should also enjoy telling you of the splendid work of Miss Louisa Lee Schuyler in rescuing 2500 pauper insane from the State poor-houses and placing them in State insane asylums where they had some chance of recovery; and of Mrs. Kinnicutt's very successful campaign to secure an efficient Street Cleaning Department. In both of these enterprises I was honored with the responsibilities of president of the Associations which the ladies organized, but the credit of these great reforms belongs entirely to them.

I must also call attention to the lion's share of the work in my report on the air of the subway, published when that public utility was first opened and certain individuals erroneously pronounced the air therein so unwholesome. Dr. Floyd J. Metzger performed the laborious portion of the investigation.

I wish I could take the time to tell you how much certain members of this Chemists' Club have contributed to the success of the City and State Health Departments: Elwyn Weller, Samuel A. Goldsmith, Edward G. Love, Arthur H. Elliott, Charles E. Munsell, and others whose names I do not just now recall.

In conclusion let me express my appreciation and warmest thanks to the members of your committee, who have considered me deserving of this Medal.

SCIENTIFIC SOCIETIES

SPRING MEETING AMERICAN CHEMICAL SOCIETY

The Spring Meeting of the AMERICAN CHEMICAL SOCIETY will be held in St. Louis, Mo., during the week of April 12, 1920, with headquarters at the Hotel Statler, Ninth Street and Washington Avenue.

The following committee has charge of the local arrangements:

Executive: DR. CHAS. E. CASPARI, St. Louis College of Pharmacy, 2108 Locust Street.

Program: DR. CHAS. E. CASPARI.

Finance: DR. F. W. FRERICHS, Herf and Frerichs Chemical Co., Pierce Building.

Hotels: DR. H. A. CARLTON, The Mallinckrodt Chemical Works, 3600 North Second Street.

Registration and Information: DR. T. R. BALL, Washington University, Skinker Road and Lindell Blvd.

Excursions: GASTON DU BOIS, Monsanto Chemical Works, 1800 South Second Street.

Transportation: DR. A. C. BOYLSTON, The Mallinckrodt Chemical Works, 3600 North Second Street.

Entertainment and Smoker: F. W. SULTAN, Sultan Drug Co., 112 North Second Street.

Banquet: E. J. SHEPPARD, National Lead Co., Manchester and Subette Avenues.

Publicity: DR. L. F. NICKELL, Monsanto Chemical Works, 1800 South Second Streets.

The University of Missouri Section, at Columbia, Mo., has agreed to act with the St. Louis Section of the SOCIETY as hosts at the Spring Meeting.

AMERICAN CHEMICAL SOCIETY'S SERIES OF TECHNOLOGIC MONOGRAPHS

At the meeting of the SOCIETY in Buffalo, in April 1919, the Committee on Publication of Compendia of Chemical Literature, etc., presented a report[1] in part as follows:

Your committee recommends that the AMERICAN CHEMICAL SOCIETY undertake to have two series of monographs prepared and published under its supervision. To give effect to this general recommendation, it would recommend that the following specific steps be taken:

(A) That three trustees be appointed, two, including the chairman, by the president of the AMERICAN CHEMICAL SOCIETY, and one by the president of the National Research Council, to organize and control the business side of the undertaking. These trustees shall be named to serve for one year and shall be eligible for reappointment. Subject to the approval of the directors of the AMERICAN CHEMICAL SOCIETY, in all matters leading to expense, the trustees shall have the power to enter into negotiations with publishing houses for the publication of the series or to develop any other plan of financial administration. In particular, it is urged that the trustees should attempt to raise funds from which advance payments of royalties (say of $500) may be made to each author (selected under B) invited to prepare a monograph and second payments of the same amount to each author when his monograph has been accepted. The trustees in return will receive all royalties accruing on the sale of a given monograph until the sums paid to an author of the monograph have been liquidated (without interest); later royalties are to go to the author. Royalties received in this way by trustees shall serve for the endowment of further monographs.

(B) That two control committees be organized, one for a series of technological monographs, another for a series of scientific monographs. Each committee is to consist of five members to be elected by the Council of the SOCIETY (as in the case of the editors of our journals). The chairman of each committee shall be the editor of the corresponding series, and shall receive compensation of the same nature as the editor of the *Journal of the American Chemical Society*. The committee shall select men who are to be invited to prepare monographs on selected topics and shall pass on the final acceptance of such monographs as may be offered for publication. Decisions as to the business arrangements for publication will rest with the trustees rather than with the scientific control committees.

The report was adopted by the Council, which authorized the Advisory Committee to elect the chairman of each board of editors. In June the Advisory Committee recommended W. A. Noyes and John Johnston as chairmen of the board of editors of the scientific and technologic series, respectively, and voted that the chairman should nominate the other members of the board. They also voted to recommend to the Directors that the salary of the chairman of each board be $1,000 a year, and that "royalties not to exceed $500 be paid in advance to each author chosen by the Committee to write a monograph, and that an additional sum of like magnitude be paid to him upon the completion and acceptance of his monograph, the amount so paid to be deducted from any royalties received until such time as the amounts advanced are returned to the Society or its agent; that thereafter any royalties received should be paid one-third to the American Chemical Society and two-thirds to the author of the monograph."

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[1] Reprinted in THIS JOURNAL, 11 (1919), 415.

On November 28 the Advisory Committee appointed as associate editors of the scientific series:

G. N. Lewis (California)
L. B. Mendel (Yale)
A. A. Noyes (Throop Inst.)
J. Stieglitz (Chicago)

and as associate editors of the technologic series:

C. G. Derick, National Aniline and Chemical Company, Buffalo, N. Y.
William Hoskins, Consulting Chemist, Chicago, Ill.
F. A. Lidbury, Oldbury Electro-Chemical Company, Niagara Falls, N. Y.
A. D. Little, Consulting Chemist, Cambridge, Mass.
C. L. Reese, du Pont de Nemours and Company, Wilmington, Del.
C. P. Townsend, Union Carbide and Carbon Corp., New York City.

They also approved a suggestion designed to insure a rotation of interests upon the Board.[1] The trustees in charge of the financial arrangements for both series are now C. L. Parsons, chairman, Gellert Alleman, and J. E. Teeple.

The board of editors of the Technologic Monographs have had considerable correspondence and have held a meeting at which the following general policy was agreed upon:

> The ideal monograph is a critical presentation of the topic which it treats, and gives the reader the present status of the knowledge of that topic in such a way that he need not consult prior literature except for details; it should show clearly which points are still uncertain and require further investigation, and so act as an incentive to research by suggesting problems. The preparation of such a monograph implies that the author has first-hand knowledge of the topic treated, and this implies in turn, particularly in the case of technologic monographs, that the topic chosen must not be too large. In other words, instead of a book dealing with a very broad general topic, we would prefer a number of more specific smaller topics, each written by a man thoroughly conversant with that particular phase. The Board wishes to emphasize that the proposed series will aim to be critical in character, rather than mere compilations; and takes this ground because a number of existing monographs cover a field broader than the author was really familiar with, the result being that the book contains one or two good chapters but is largely a somewhat uncritical compilation of material.

Before authorizing monographs the Board wishes to review the whole field carefully; to ascertain what topics have already been treated adequately in readily available monographs; and to prepare a systematic well-balanced scheme covering the area of desirable effort, indicating the relative importance of subjects or the relative need of treatment. However, where an author is available who is uniquely qualified to treat a particular subject within our scheme, we should get a monograph from that man while he is available and not run the risk of losing the benefit of his special knowledge, and should do so without much reference to the order in which we would otherwise take up the subject if it were one in which a reasonable number of fully qualified men were available.

It is realized that the main difficulty is likely to be to secure the author best qualified to write on a particular topic—especially in view of the policy of secrecy which has prevailed in so many instances—and that the selection of topics will be largely determined by the availability of an appropriate author. The difficulty likely to be encountered in securing a good monograph dealing with a specific manufacture inclines the Board to the belief that it might well give preference to monographs dealing with general operations, such as drying, roasting, grinding, mixing, filtration, etc., until these unit operations, which constitute the elements of technologic chemical processes, have been fairly well covered. Among the topics already suggested as desirable, the following may be mentioned: industrial hydrogen, corrosion of metals, resistant alloys, water softening, pyrometry, liquefaction of gases, catalytic and electrolytic oxidation and reduction of organic compounds. In all cases it is proposed that the manuscript, before it is accepted for publication, shall be reviewed by at least one man who is thoroughly conversant with the particular topic.

It is hoped that a definite program may be formulated within the next two months, so that the books may begin to appear in the fall. In the meantime the Board invites the membership of the Society to coöperate by favoring it with comments and suggestions, particularly with specific suggestions of desirable topics and competent authors. All correspondence relative to the technologic series should be addressed to John Johnston, Yale University, New Haven, Conn.

THE A. C. S. NEWS SERVICE REPORT

The remarkable interest and coöperation which the press of the United States has shown in the work of the A. C. S. News Service of the American Chemical Society are indicated in the analysis of the newspaper clippings which we received in the last year.

There were issued in 1919, 35 bulletins, from which 893 clippings were received, as compared with the 54 bulletins issued in 1918, from which 455 clippings resulted. The space occupied by the clippings received in 1919 amounts to 7,768 inches as compared with the 3,319 inches of the previous year. These returns indicate only in a general way the extent to which the Service has been received, as there is no method by which an absolute check can be made on the volume of publicity of this character.

The Service now supplies popular information on chemistry to 650 newspapers and magazines, for in August of last year the publicity list was practically doubled. Of the newspapers in the United States, 205 print our bulletins with the regularity of clockwork, while others select from time to time those which are of special interest in their localities.

The most significant development of last year was in connection with the meetings of the Society. As the two meetings of the year constitute the most important news points with which our Service has to deal, an effort was made to bring them especially to the attention of the press. The Cleveland meeting, held in the fall of 1918, had practically no publicity—possibly not more than 10 or 15 notices in all. Although our resources did not permit a full program in connection with the Buffalo meeting, held in 1919, we obtained a limited amount of notice for that gathering in American newspapers. The Buffalo papers printed 67 news items concerning the spring meeting of 1919, and 35 appeared in other newspapers throughout the United States.

The fall meeting of 1919, held in Philadelphia, gave an opportunity to test the value of a national publicity program—the first ever undertaken by this Society. This was possible through the enterprise of the Philadelphia Section, which paid the entire expenses. The Associated Press, the United Press, the International News Service, the Western Newspaper Union and various agencies coöperated with the A. C. S. News Service in distribution. The result was that every newspaper of importance in the United States gave adequate reports, and 20 publications sent special representatives to cover the meeting. A press room was established at the Hotel Bellevue-Stratford and every facility was placed at the disposition of reporters and correspondents. The matter distributed there was equal in words to 30 of our weekly bulletins.

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[1] This Journal, 12 (1920), 84.

A preliminary publicity campaign of six weeks, undertaken to stimulate the interest of the American people, reached its climax on the first of September 1919. The clipping book now in the possession of the Philadelphia Section shows 700 notices of the meeting of last autumn, exclusive of those obtained from the regular bulletins.

Success of the pre-publicity has caused the Director of the Service to continue the policy of having an extensive advance campaign.

Another important development of the A. C. S. News Service was the coöperation which it received from the local sections. The secretaries of a number of the sections have been in close touch with the newspapers of their localities, and from that policy has developed important auxiliary publicity. The clippings containing accounts of meetings of local sections form very gratifying evidence of the increased popular interest in chemistry which has been stimulated by this means throughout the United States.

In addition to the bulletins and other matter, clip sheets were sent out in 1919 for the first time, on which were important articles from the *Journal of Industrial and Engineering Chemistry* and also its editorials. The ten sheets mailed were well received by the newspapers—so much so as to lead us to extend this Service in 1920 by re-writing some of the articles into popular form, and making a general revision of the clip sheet along newspaper lines.

In view of the progress made by the A. C. S. News Service, the Directors decided to increase the appropriation made for the year 1919; to generally increase the facilities; and to provide for systematic programs covering the spring and fall meetings.

The policy of national publicity inaugurated at the Philadelphia meeting in September 1919 will be continued and developed at the New York office, with the assistance of the local sections.

The bulletins will be increased so that, besides a general one each week, there will be also issued, from time to time, special bulletins applying to definite parts of the country or of interest to groups of newspapers and magazines.

As some of the newspapers have already availed themselves of our offer to advise them on the scientific accuracy of articles on chemistry in advance of publication, we shall extend this method of serving them for the coming year.

From small beginnings the Publicity Service of the AMERICAN CHEMICAL SOCIETY has now grown to large proportions and is recognized by the journalistic world as a valuable source of news and information.

JOHN WALKER HARRINGTON,
Technical Manager

NEW YORK, N. Y.
January 1, 1920

ROCHESTER SECTION, AMERICAN CHEMICAL SOCIETY

At a recent meeting of the Rochester Section, at which Secretary C. L. Parsons was present, the local membership committee had made a careful canvass of the chemists around Rochester and presented to the Secretary at one time forty-two new members. Most of these new members were present at the time their names were read, and the Secretary signed their applications as each one stood up in the audience.

CALENDAR OF MEETINGS

American Ceramic Society—Annual Meeting, Hotel Bellevue-Stratford, Philadelphia, Pa., February 23 to 26, 1920.

American Electrochemical Society—Spring Meeting, Boston, Mass., April 8 to 10, 1920.

American Chemical Society—Fifty-ninth Meeting, Hotel Statler, St. Louis, Mo., April 12 to 17, 1920.

NOTES AND CORRESPONDENCE

EXPLAINS DANGER OF WOOD ALCOHOL[1]

DR. REID HUNT, EMINENT AMERICAN AUTHORITY ON EFFECTS OF ALCOHOL, SHOWS DIFFICULTIES OF DETECTING POISON DRINK AND EXPLAINS FACTS CONCERNING IT UNKNOWN TO THE GENERAL PUBLIC

NEW YORK, DECEMBER 31, 1919—Facts concerning the dangers of wood alcohol which are scarcely known to the general public were given to-day by Dr. Reid Hunt, a leading American authority on the effects of alcohol, whose researches in this line are regarded as having been more extensive than have those of any other American scientist.

Dr. Hunt is the head of the Department of Pharmacology of the Medical School of Harvard University, was formerly at Johns Hopkins, and several years ago was chief of the Division of Pharmacology of the United States Health Service, in which position he advised the Government in the regulation of the sale of drugs, poisons, and intoxicating liquors. He is the author of the standard work, "Studies in Experimental Alcoholism." At the request of the AMERICAN CHEMICAL SOCIETY, of which he is a member, Dr. Hunt prepared a bulletin on wood alcohol. To-day this was given out for publication.

"Wood alcohol," writes Dr. Hunt, "has become known as the American poison on account of the frequency with which cases of poisoning have been traced to it in the United States. Despite this fact, there is still a lack of appreciation of its dangers and of an understanding of its nature. It is on this account that I am glad to comply with the request of the AMERICAN CHEMICAL SOCIETY to prepare this bulletin. The misconception of the dangers of wood alcohol evidently exists not only among those who drink or sell 'alcoholic' beverages of unknown origin, but also to those who prepare drinks containing wood alcohol for sale and perhaps also to those who sell wood alcohol to the latter class. No other explanation of the recent accidents is thinkable; for, however sordid the motives and however reckless of human life the manufacturers of spurious 'alcoholic' beverages may be, it is unreasonable to suppose that anyone would knowingly incur the legal and other responsibilities for such a wholesale slaughter as has recently taken place."

POPULAR MISCONCEPTIONS

"Among the misconceptions prevalent," said Dr. Hunt, "the following may be mentioned:

"Many consumers and perhaps some of those who sell such drinks seem to think that wood alcohol has such characteristic properties that its presence can be readily detected by the odor or taste. On the other hand, those who make such drinks know that this is not the case, but believe either that the poisonous action has been exaggerated or that the chances of detection are relatively slight.

"Moreover, testimony was offered in a court a number of years ago to the effect that the manufacturers of flavoring extracts had been approached by dealers in wood alcohol and urged to make their preparations with it. The fact that already at that time the bottles bore the label 'poison' was explained as a ruse to prevent the Government from placing an internal revenue tax upon wood alcohol.

"It cannot be too strongly emphasized," he added, "that there is not a single property of wood alcohol, except its poisonous effects, by which anyone but a chemist can distinguish between purified wood and ordinary or 'grain' alcohol. The appearance, odor, and taste of the two are so strikingly alike, that even chemists who have had much experience with them are unable by these properties to distinguish between them with certainty. The difficulty is, of course, greatly increased when essences, flavors or coloring matters are added, as is the case in the spurious drinks now being offered for sale. Not only can the consumer, however great his familiarity with alcoholic beverages may be, not trust his own judgment in this matter but he cannot trust the judgment of an experienced bar or saloon keeper.

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[1] A. C. S. News Service Bulletin issued to the press for release on January 1, 1920.

HOW WOOD ALCOHOL POISONS

"Now, as regards the question of the poisonous properties of wood alcohol," added the expert:

"It is inconceivable that any ordinarily intelligent person can now be in doubt on this subject, in view of the hundreds of cases of death and blindness resulting from its use. Twenty years ago when such cases first began to be reported there was some reason for a little uncertainty on this subject, not only on the part of the public, but of chemists and of those physicians who were not familiar with certain pharmacological experiments on dogs. The odor, taste, and other properties of pure wood alcohol are so like those of ordinary alcohol that chemists were inclined to attribute the bad effects from the former to the presence of impurities in the commercial samples. But none of the impurities in the latter are as poisonous or cause the same effects as the absolutely pure wood alcohol itself.

"Pharmacologists, moreover, from experiments on dogs, had, years before, shown that the action of wood alcohol upon the animal organism is fundamentally different from that of ordinary alcohol. This difference may be briefly summarized. When ordinary alcohol is taken into the body it is rapidly converted into water and carbonic acid gas which are harmless substances, always present in the body, and any excess of which is promptly eliminated by the kidneys and lungs. Wood alcohol, on the other hand, instead of being changed into harmless substances which are easily eliminated, remains in the body as such for a considerable time and is then slowly converted into another poison—formic acid—the acid which is found in ants. These poisons and perhaps a third formed from the wood alcohol, formaldehyde, attack the brain and other organs and cause death or blindness.

"Poisonousness is an inherent quality of wood alcohol," continued Dr. Hunt. "It is as impossible to prepare nonpoisonous wood alcohol as it is to prepare nonpoisonous prussic acid.

HOW MUCH IS A FATAL DOSE

"Individuals vary considerably in their susceptibility to wood alcohol; some die or become blind from amounts which seem to do no harm to others. This is true, however, of all poisons. Death or blindness has resulted from two teaspoonfuls and from one or two tablespoonfuls of the poison. Sixty to seventy-five per cent of those taking four ounces, that is, a quarter of a pint or half a 'glassful,' have died or become permanently blind. That wood alcohol is properly placed in the list of 'deadly poisons' is evident from the fact that the mortality from arsenic poisoning is only fifty to seventy-five per cent and that from bichloride of mercury even less. Of a group of 130 men who drank a mixture of wood and grain alcohol all but 32 died or became blind.

"At the present time when the manufacture and sale of genuine alcoholic beverages are illegal the only safe course to pursue is to refrain from buying, drinking, or dealing in anything purporting to be such a beverage.—[*Bulletin* **251**]

REGISTRATION OF STILLS

A question has been raised as to whether the law requiring registration of stills applies to distilling apparatus used in chemical work.

A notice issued by the Commissioner of Internal Revenue reads in part as follows:

To Collectors of Internal Revenue, Revenue Agents, and Others Concerned:

* * * * All persons, firms or corporations thus manufacturing a still or worm to be used in distilling are deemed manufacturers of stills. This applies to all stills capable of the production of distilled spirits but does not apply to small laboratory stills (usually glass) for legitimate laboratory purposes, or to water stills which are not capable of and intended for the production of distilled spirits. Ordinarily, laboratory stills are small, constructed of glass, and not adapted to the production of distilled spirits in commercial quantities, and many water stills are also of such construction that they are not adapted to the commercial production of distilled spirits.

Any stills or worms adapted to the production of distilled spirits for commercial or beverage purposes are presumed to be intended for such use. * * * In order to remove such presumption in the case of stills and worms intended to be used in the manufacture of essential oils, vinegar, and like products, and in purification of water (other than small glass laboratory stills), the person for whom such still is made will be required to submit to the Collector evidence under oath showing that the still is not to be used for the production of spirits and setting forth specifically the actual purposes for which it is to be used.

* * * *

All stills set up, whether intended for use or not, must be registered with the Collector of the district on Form 26 in duplicate. This applies to all stills of whatever size or for whatever purpose intended, whether for distillation of spirits or for pharmaceutical or other purposes, except as to small glass laboratory stills.

Copies of Form 26 may be obtained from the Collector of Internal Revenue for the district in which the stills are to be set up, and instructions will be given as to filling out such forms. Failure to register such still or distilling apparatus will be a violation of Section 3258 R. S.

EXTRACT FROM THE FEDERAL LAW RELATING TO THE REMOVAL OF THE "COUNTRY OF ORIGIN" FROM IMPORTED ARTICLES

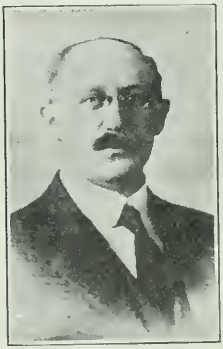
United States Tariff Act of 1913, Sec. 4, Par. F, Subsection 2

If any person shall fraudulently violate any of the provisions of this act relating to the marking, stamping, branding, or labeling of any imported articles or packages; or shall fraudulently deface, destroy, remove, alter, or obliterate any such marks, stamps, brands, or labels with intent to conceal the information given by or contained in such marks, stamps, brands, or labels, he shall upon conviction be fined in any sum not exceeding $5,000, or be imprisoned for any time not exceeding one year or both.

DISAPPEARANCE OF DR. ARTHUR LACHMAN

The disappearance, on December 11, 1919, of Dr. Arthur Lachman, of San Francisco, was noted in the last number of This Journal. The causes suggested are foul play or temporary dementia.

The accompanying description and photograph are printed here in the hope of developing some clue.



Arthur Lachman

Address: 358 Holbrook Building, San Francisco, Cal.—Sutter 4653; 143–14th Avenue—Pacific 3926.

Height: 5 ft. 7 in.

Weight: 170 lbs.

Complexion: Fair

Eyes: Light blue

Hair: Very bald—gray. Reddish mustache, turning gray

Glasses: Wore eye glasses

Clothing: Gray-green suit, small plaid
- Black vici kid shoes
- Dark gray, knee-length overcoat
- Dark fedora hat

Effects: Pipe; curve cut old English tobacco
- Illinois watch
- Black silk vest chain, initial slide, letter "L" set in pearls
- Gold cuff buttons each set in one diamond and one ruby
- "Lefax" memorandum book

ADVANCED WORK FOR HIGH SCHOOL CHEMISTRY TEACHERS

Editor of the Journal of Industrial and Engineering Chemistry:

From time to time articles have appeared in various chemical journals advocating more thorough training for men in chemical professions. A great deal has been said about chemists doing advanced work and in a number of instances provision has been made whereby men with certain companies have been provided with means for development along research lines.

I feel that something should be said in regard to the teachers of chemistry in the various high schools over our country. A university professor of national reputation made the remark at a scientific meeting not long ago that some of the best material available for replenishing the staffs of various universities was to be found in the men who are teaching in the high schools. If this is the case, why not give these men a chance to earn a doctor's degree, which is now required to hold a position with most, if not all, of the foremost colleges and universities? Men in high schools who are heads of departments, especially in large cities, receive salaries ranging from $3,000 to $4,000 per year of 10 mos. In most cases they have their bachelor's and master's degrees, have done graduate work beyond this, and very often keep in touch with the chemistry department of some good university.

These men would like to go on and obtain the doctor's degree, but such a thing is impossible under present conditions, unless the applicant for the degree resigns his position in his school and spends a year or more at the university. Some compensation indeed may be obtained by instructing part time and devoting the remaining time to the problem at hand, but they have assumed responsibilities for which such compensation is inadequate, and few are going to relinquish salaries of $3,000 a year and spend $2,000 more per year to keep their families, in order to obtain the degree.

Why not offer some alternative? Permit them to use their spare time during the academic year in their own laboratories on some assigned problem, especially where library and laboratory facilities are quite complete, and then have them come to the university during the summer to continue the work and so on for the following years until all requirements for the degree are fulfilled. This suggestion, if followed, would eliminate some of the longer graduate courses, but certainly not all of the graduate courses.

If this, or some other plan, be adopted it would enable these men to go into college or university work when the degree was obtained, and there is no reason to believe that they would fall short of what is expected of them. When, in this way, they have become eligible for positions in a university at a salary even somewhat less than they are now receiving, the university would be able to replenish its corps with experienced teachers, instead of graduate students with no teaching experience. It is not necessary, however, that these men go into university work. They may remain where they are. It is a well-known fact that a great deal of research work has been done in other countries by men in secondary schools. Let it be so in this country. All that is needed is a little encouragement.

Personally, I feel that the time is coming when universities will make provision for these science men. When they do it certainly will stimulate every red-blooded man to put forth the best that is in him and will open a field rich in scientific workers which at present is practically inactive.

Soldan High School
St. Louis, Mo.
January 5, 1920

W. R. Teeters

THE QUESTION OF THE IDENTITY OF BALATA AND GUM CHICLE

Editor of the Journal of Industrial and Engineering Chemistry:

With reference to my paper on "Industrial and Agricultural Chemistry in British Guiana, with a Review of the Work of Prof. J. B. Harrison" [This Journal, 11 (1919), 874], I have received several inquiries as to balata and whether or not it is the same substance as gum chicle. My impression had always been that the two substances were derived from different trees but to be certain I referred the query to Professor Harrison, who writes as follows:

> Balata and true gum chicle are not identical. Your impression that they are derived from different trees, the *Mimusops balata* and the *Sapota zapotilla*, respectively, is correct. But quite recently an export trade has arisen from Venezuela in what the Creoles call "white hya-hya" and the Venezuelans term "white balata," the impissated latex of the "milk" tree. This is being used either directly as chewing gum or else as an adulterant of chicle. The latex of certain ficus trees termed locally *douchallibali* and *kumatraballi* is probably also being used as adulterants of chicle.

Balata and gum chicle are treated as synonymous terms in the Decennial Index of *Chemical Abstracts*, but as pointed out by Professor Harrison the two substances are not identical and they should, therefore, have been treated in the Index under separate headings.

C. A. Browne

New York Sugar Trade Laboratory, Inc.
80 South Street, New York, N. Y.
January 6, 1920

PLATINUM THEFT

On Monday morning, December 22, 1919, it was discovered that the vault of the Department of Agricultural Chemistry at the University of Missouri had been entered and the entire stock of platinum crucibles, amounting to some 2500 g., had been taken. The following list is a fairly accurate inventory of the material taken:

	Grams
18 plain crucibles 6 J. Lawrence Smith crucibles 11 Gooch crucibles	780.38
27 dishes	1212.72
Foil	26
Wire	17
5 small, flat, sugar dishes	77
17 Gooch crucible caps	41.5
6 small caps	10.5
21 seamless filter cones	73
18 covers for crucibles	96
6 covers for dishes	43
2 spatulas	12.5
2 spoons	6.5
Scrap	22.2

FIRE CAUSED BY YELLOW PHOSPHORUS

In the rubbish from a fire which occurred in the chemical stock shelves of the Organic Research Laboratory, a can was found partly filled with yellow phosphorus. This had been in stock for approximately five years. The cover had been forced open about one-sixteenth of an inch, and the bottom had numerous pinholes. Presumably these had been formed by corrosion with the result that the water leaked out very slowly. A slow oxidation of the phosphorus then took place, becoming more rapid as the temperature rose. Finally sufficient pressure was developed to force open the cover and the phosphorus then burst into flames. A close watch should be kept on stocks of yellow phosphorus in cans, or else the contents transferred to glass bottles and covered with water, the bottles then being securely stoppered. The manufacturers should attempt to find some better method of packing the substance.

Harry LeB. Gray

Organic Research Laboratory
Eastman Kodak Company, Rochester, N. Y.
December 23, 1919

RESEARCH ON METALLO-ORGANIC COMPOUNDS AT NORTHWESTERN UNIVERSITY

Northwestern University's Department of Chemistry has received a grant of $3,500 from the Interdepartmental Social Hygiene Fund of the United States Government. This fund is for the purpose of supporting research leading to the development of new metallo-organic compounds which may prove of therapeutic value in the treatment of syphilis of the central nervous system.

A plan of coöperation has been worked out between the Universities of Wisconsin, Minnesota, Illinois, and Northwestern, whereby all pharmacological work will be done by the first-named institution and the synthesis of new compounds by Minnesota, Illinois, and Northwestern in coöperation.

WASHINGTON LETTER

By J. B. McDonnell, Union Trust Building, Washington, D. C.

The middle of January finds the fight in the Senate over the protection of the American dye and coal-tar chemical industry still unsettled. The Longworth dye bill which was passed by the House and which will serve as the basis for whatever measure the Senate passes, is before the subcommittee of the Senate Finance Committee, which has not yet agreed as to just what shall be the provisions of the measure it finally will frame.

Members of the committee say they probably will have a measure ready for the Senate within the next fortnight. A meeting of the dyes subcommittee will be called some time next week to consider the measure in the light of hearings which have been held, and a report is expected soon thereafter.

Faced with a strong opposition from some members of the Senate to the licensing system as embodied in the Longworth bill, the dye men have drafted a substitute for this section and the licensing system, as such, is discarded. The committee now has before it this substitute; another offered ostensibly by John P. Wood, of Philadelphia, one of the leading opponents of the Longworth bill both before the House and Senate committees, and other tentative suggestions from various quarters. These two are the most important and from them probably will come the measure which the committee will decide on.

The substitute which was drawn up by a committee of the American Dyes Institute and submitted to the committee by Joseph H. Choate, Jr., counsel, provides in brief:

> That the United States Tariff Commission shall prepare two lists, one list of dyes and coal-tar chemicals covered by the act, to be known as the importable list, and a second to be known as the conditionally importable list. Products not on either of these lists could not be imported. The provisions would remain in effect for a period of ten years.

The proposed substitute, as submitted to the committee, follows:

> Sec 503. (*a*) During 10 years after the taking effect of this act, no product covered by the dutiable list in Section 500 hereof which is manufactured in the United States in quantity sufficient to meet the demand for domestic consumption, and in quality substantially equal to the standard for such product, prevailing in the industry on August 1, 1914, and no product having substantial usefulness only as a substitute for a product so manufactured in the United States, shall be admitted to import. All questions of fact as to which of such products are entitled to admission to import shall be determined by the United States Tariff Commission as hereinafter provided.
>
> The said Tariff Commission shall forthwith proceed to prepare after investigation, a list to be known as the importable list of such products as may be found by it to fulfill the above requirements for admission to import. The said list shall be revised from time to time, and except as hereinafter provided no product not named thereon shall be admitted to import.
>
> Before any of the products named on said list shall be admitted to entry, the importer shall file with the Tariff Commission a notice containing sworn statements by the importer that the proposed import is either for current use or consumption by him and will not, either alone or in conjunction with previous notice, or any other supply from whatever source derived, suffice to provide him with a quantity greater than his actual requirements for such current use or consumption for the ensuing six months, or that the proposed import is desired in order to fill an actual *bona fide* order from a named domestic consumer for such consumer's like current use or consumption, in which event there shall be annexed to the notice proof by affidavit of such consumer that the proposed import will not either alone or in conjunction with previous orders or any other supply from whatever source derived, suffice to provide him with a quantity in excess of his actual requirements for such current use or consumption for the ensuing six months. Said sworn statement of the importer shall also state the name, chemical identification, strength and quantity of the proposed import, together with the name of the port of entry at which it is to be brought in. A copy of such notice shall be transmitted by the commission to the collector of said port, and no import shall be admitted to entry unless found to correspond with such notice. The collectors of all ports shall promptly notify the Commission of the admission of all such imports. The phrase "use or consumption" as used herein shall, in the case of products customarily used for medical or photographic purposes only, include sale for such purposes only. The Commission may suspend, pending investigation by it, the operation of any notice which may appear to it to be calculated to provide any consumer with a supply of any product in excess of his actual requirement for current use of consumption during six months after the date of such notice If upon such investigation the Commission shall determine that any such notice covers any such excess, it shall forthwith cancel the said notice and notify the person by whom the same was filed.
>
> When at any time the Commission shall find that notices received by it, of which copies have been transmitted to the collectors, cover a quantity of any product sufficient in the aggregate to constitute an excess over current consumption equal to a six-months' supply for the ordinary requirements of such product for domestic consumption, no copies of notices covering such product shall be transmitted to the collectors until the commission shall determine that the unused quantity of such product in the United States is less than such six months' supply The Commission shall promptly notify of such action all persons who have filed notices the operation of which is thus suspended
>
> The Commission shall also prepare a second list to be known as the conditionally importable list comprising all products which, while mainly useful as substitutes for domestic products, have special uses for which a domestic equivalent is not available. The said conditionally importable list shall state opposite the name of each product the special uses. Any product named in such list may be imported, subject to the conditions hereinbefore provided, when and only when the notice covering the proposed import contains a sworn statement by an actual consumer that the proposed import will be used by him solely for one or more of the special uses stated in said list for said product.
>
> Notices received by the Commission shall not be open to public inspection.
>
> If at any time complaint shall be made of the Tariff Commission that the price of any domestic product covered by the dutiable list of Section 500, of this act, is unreasonably high, the Commission shall investigate and if upon such investigation the Commission shall, after a hearing, determine that such price is sufficient to yield an unreasonable profit to every domestic manufacturer, it shall place such product on the importable list during the continuance of such unreasonable prices. Two weeks' notice of such determination shall be given all domestic manufacturers of such product known to the Commission before such product shall be placed on the importable list.
>
> Notwithstanding anything herein contained, any product covered by this act may be imported and stored in a United States bonded warehouse. No product so imported shall be released from such bonded warehouse or admitted to entry except as hereinbefore provided.
>
> Sec. 503. (*b*) The United States Tariff Commission in executing the duties imposed upon it by this act may regulate its own practice and procedure, but shall so regulate the same as to prevent all avoidable delay.
>
> Sec. 503. (*c*) Any product covered by Section 500 of this act, which shall be imported into the United States or any of its possessions, otherwise than as provided herein, shall be forfeited and shall be destroyed whenever and wherever found.
>
> Sec. 503. (*d*) Any person subject to the jurisdiction of the United States who shall, either as principal or as accessor, import or attempt to import or aid in importing any product covered by Section 500 of this act, otherwise than as herein provided, or who in making any sworn statement required by this act shall willfully misstate or misrepresent any facts shall be fined not exceeding $5,000 or the value of such product at the time of importation, whichever shall be greater, or shall be imprisoned for not more than one year, or both.
>
> Sec. 504. Except as otherwise herein specially provided, this act shall take effect on the day following its passage.

Committee members who have expressed themselves as being opposed to the licensing system agree that the substitute quoted above is an improvement, and some have expressed the opinion that with modifications this will be written into the bill in place of the licensing provision. Objection is found to the length of time—ten years—it is proposed to continue the law in effect. This very probably will be reduced.

Another objection which has been raised is that under its provisions American manufacturers may be exporting products which consumers are not permitted to import. Some dissatisfaction has been expressed with the six-months' supply provision, also.

An attempt to forecast just what the committee will do is futile. Frankly, members of the committee do not know themselves. The plan offered by John P. Wood has found some favor. This is not actually Mr. Wood's plan but was drawn up by an official of the Tariff Commission. As first drafted it was rather lengthy and when submitted to one of the influential members of the committee it was suggested that it be rewritten, much of the lengthy definitions contained in it eliminated, and the proposal be boiled down.

This was done and the plan was submitted to the committee by Mr. Wood at the hearings which were reopened for a day on January 12.

The products of any firm or individual who engaged in full line forcing, tying contracts, or unfair competition, could be prohibited from import by the customs officials under this plan The first paragraph is as follows:

> Sec. 504. Whenever it shall appear to the satisfaction of the United States Tariff Commission (*a*) that any person is commonly and systematically importing, selling, or causing to be imported and sold any products enumerated in Section 500 of this act under any agreement, understanding, or conditions that any persons shall not use, purchase, or deal in, or shall be restricted in his using, purchasing, or dealing in such products of any persons, or (*b*) that any person is guilty of any other unfair method of competition in importation of products enumerated in Section 500 of this act, said Commission shall certify that fact to the Secretary of the Treasury, and entry into the United States shall thereupon be refused to any such products, sold, shipped, consigned, or manufactured by such person: PROVIDED, That such act or acts shall be done with the intent, tendency, or result of destroying or injuring any industry in the United States or of preventing the establishment of an industry in the United States or of restraining or monopolizing trade and commerce in the United States.

The substitute amendment offered by the dyes committee aims to prevent the possibility of harm being done to the American coal-tar chemical industry by restricting imports. That offered by the Tariff Commission through Mr. Wood is designed to punish those who do harm to the industry. The former anticipates and moves to prevent; the latter waits until harm is done and then seeks to punish.

These two proposed amendments were discussed at the brief hearing held by the committee on January 12, at which Mr. Choate testified for the dye industry; while Mr. Wood, Herman A. Metz, and several other consumers and importers also were present.

The Tariff Commission discusses the various methods of protecting the industry which have been suggested in a report on the Longworth bill which it has submitted to the Senate Finance Committee. This report deals with administrative difficulties foreseen if some of the proposals before the committee are enacted and seeks to perfect them, urging the wisdom of Congress fixing "the governing rules" so that the administrative body enforcing the law will not be required to initiate policies.

Attention also is directed to "the exceedingly complex administrative problems connected with undertaking to determine, as the bill requires, what will be reasonable terms as to prices, quality and delivery of domestic dyes, in the absence of which the importation of foreign dyes may be licensed." The report deals largely with the licensing system, and many of the difficulties pointed to in it are removed in the substitute offered through Mr. Choate. The report suggests:

> It is further suggested that the proposed legislation does not at present take account of the fact that many licenses which may be granted by the license authority may be rendered inoperative through the control of numerous German patents, sold by the Alien Property Custodian during the war to the Grasselli Chemical Company, of Cleveland, Ohio, and to the Chemical Foundation. The Tariff Commission suggests that Congress may find it possible before enacting the legislation to secure from these corporations binding agreements to issue licenses under their patents, without discrimination and at definitely stated rates, to all recipients of import licenses.

Francis P. Garvan, president of the Chemical Foundation, Inc., told your correspondent that the Foundation would immediately comply with any request which may be made of it along this line, when informed of the suggestion of the Tariff Commission.

The measure for the protection of the dye and coal-tar chemical industry which seems most likely to be decided on by the committee at this time, is a compromise between the two substitutes. The dye industry is having a harder fight in the Senate than in the House. It needs a Longworth in the Senate. What the outcome will be is still a secret of the future.

While some members of Congress have expressed opposition to the proposal to establish the Chemical Warfare Service as a separate unit of the War Department, the majority sentiment among committee members who have the reorganization measures in charge, seems to be in favor of such a proposal, recognizing the extreme importance of this branch in future warfare.

Reports reaching here from abroad state that the German chemical trust is taking steps to double its capital. Belief is expressed in England, it is said, that in spite of all difficulties, Germany is in better position as regards this industry than ever before.

January 15, 1920

INDUSTRIAL NOTES

On January 1, 1920, The Norvell Chemical Corporation of Perth Amboy, N. J., was incorporated in Delaware with an authorized capital of $1,000,000 of preferred stock and 20,000 shares of common stock, no par value. The company has taken over from McKesson & Robbins, Inc., property near Perth Amboy, N. J., consisting of 350 acres of land and a number of factory buildings, and will operate the plant, supplying the medical profession and the drug trade with pharmaceutical chemicals and the industries with chemicals useful in the manufacture of a variety of products. The company has a staff of highly trained chemists for research work. At a stockholders' meeting the following directors and officers were elected: President, Donald McKesson; Vice President and Treasurer, Saunders Norvell; Second Vice President, Francis J. McDonough; Secretary, William S. Gray, Jr.; Assistant Treasurer and Assistant Secretary, James J. Crawford; General Manager, George Simon.

The Bureau of the Mint and the Geological Survey have issued the following preliminary estimate of the production of gold and silver in the United States during the calendar year 1919: Gold, 2,829,395 oz., valued at $58,488,800; silver, 55,285,196 oz., valued at $61,966,412. These figures, compared with those for 1918, show a reduction in the output of gold of $10,157,900, and in that of silver of 12,524,943 oz.; compared with those for 1917 they show a reduction in gold of $25,261,900, and in silver of 16,455,166 oz.

Platinum and gold worth $75,000 were stolen on December 28, 1919, from the plant of the Roessler & Hasslacher Chemical Co., Perth Amboy, N. J. Burglars drilled the safe.

The Director of Sales of the War Department has announced that the Ordnance Department Salvage Board, through the District Office, 1107 Broadway, New York City, is offering for sale land, buildings, and equipment of the sulfuric acid plant at Mount Union, Pa. The plant consists of two brick buildings and several frame buildings, and the land comprises $20^1/_2$ acres. Among the facilities are 784 yards of railroad siding, 1,887 ft. of 8-in. water main, sewers, electric lights, and roads. The equipment includes 4 improved rotary burners, 2 sulfur elevators, 4 Boston type gas pumps, and a 100-ton, 50-foot Howe truck scale, all ready for immediate shipment.

A test case brought by the United States Department of Agriculture against the Monsanto Chemical Works for shipping saccharin has ended in a disagreement of the jury. The case has been pending since 1916. The Monsanto Chemical Works requested another trial immediately, but the government attorneys refused to try the case again until the next term of court, some months from now.

The Engineering Experiment Station of the University of Illinois has sixteen research graduate assistantships open to graduates of approved universities and technical schools for research work in engineering, physics, and applied chemistry. Appointment must be accepted for two consecutive collegiate years, at the end of which the Master of Science degree will be conferred if all requirements have been met. Assistantships carry $500 stipends and are free from all fees except matriculation and diploma fees. Application must be made to the Director not later than the first day of March, to become effective the following September.

Announcement has just been made of a contribution of $5,000,000 by the Carnegie Corporation of New York for the use of the National Academy of Science and the National Research Council. A part of the fund will be used for erecting in Washington a home for the two beneficiary organizations. The remainder will be placed in the hands of the Academy, which possesses a federal charter, to be used as a permanent endowment for the National Research Council.

The Bureau of Chemistry of the U. S. Department of Agriculture has announced the production of malt sugar sirup on a commercial scale as a substitute for sugar. Both the raw materials and the machinery formerly used in the manufacture of beer can now be used for the production of malt sugar sirup, and up to a certain point the process is the same. Malt sugar sirup has a flavor very like honey and can be used wherever cane sugar is used.

The *Journal of Commerce* reports the development in England of a new process for the extraction of commercial alcohol, which though still in the experimental stage, is said to be a perfect motor spirit. Ethylene, alcohol and derivatives have been extracted from coke oven gas by the sulfuric acid contact process on a commercial scale, at the Skinningrove Iron and Steel Works, giving an average yield of 1.6 gallons of alcohol per ton of coal carbonized. According to calculations, all the coal reduced to coke in England in 1918 would have produced over 23,000,000 gallons of alcohol, had this process been applied.

The United States Civil Service Commission announces a competitive examination for research chemist for work in connection with iron and steel or refractories and gases, at a salary of $2,200 to $2,500. Applications must be filed with Civil Service Commission, Washington, D. C., by February 10, 1920.

The United States Civil Service Commission announces an examination for pyrotechnic engineer at a salary of $2,400 to $3,600 Applicants must have graduated in mechanical, electrical, or chemical engineering from a college of recognized standing and have at least one year's experience in engineering and aviation work. Applications must be filed with the Civil Service Commission, Washington, D. C., by February 17, 1920.

The Duane Sugar Refining Co., of Connecticut, recently incorporated with capital stock of $500,000, has bought the plant at Waterside, Conn., formerly occupied by the Synthetic Color Company and later by the Edgewood Arsenal, and will equip a sugar refinery for the Stollwerck Company and allied industries.

New trade names have arisen for vat dyes in England. The vat dyes of British Dyes, Ltd., are called chloranthrene colors; those of Levinstein, Ltd., duranthrene colors; those of L. B. Holliday & Co., hydranthrene colors; while Scottish Dyes, Ltd., has affixed the name of caledon to its products.

Among the corporations recently formed for the production of chemical products are the following: Egyptian Chemical Co., Boston, Mass., capital $90,000; Shawinigan Products Corporation, Manhattan, capital $200,000—carbide, acetic acid and chemicals; California Chemical Co., Dover, Del., capital $1,000,000; Dura Chemical Co., Philadelphia, Pa., capital $100,000—dyestuffs and chemicals; Exidol Laboratories, Inc., Dover, Del., capital $100,000; The Yardley Chemical Corporation, Manhattan, capital $450,000.

During the first nine months of 1919 about 40,400 oz. of platinum were imported. According to James M. Hill, of the United States Geological Survey, Department of the Interior, there seems to be little hope of any marked increase in the output of platinum in the United States or Canada over the small output heretofore made.

The Iowa Corn Products Company has been reorganized with an initial capital of $1,000,000, which will be increased, and has effected a permanent organization with the following officers: President, O. J. Meredith; Vice President, A N. Higgins; Treasurer, F. T. Fogarty; Secretary, R. B. McConologue. T. C. Cessni will be chairman of the board of directors.

In its third annual report submitted to Congress with the close of 1919 the United States Tariff Commission outlines the work of the Commission on acids dutiable under paragraph 1 of the tariff act of 1913, as well as the raw materials from which such acids are made, and several closely allied commodities which are dutiable under other paragraphs. This report will soon be available for distribution. The list includes formic, oxalic, citric, tannic, gallic, pyrogallic, and tartaric acids, which present tariff problems of a most varied character. In several cases there were notable developments of the industry in the United States during the war. This was particularly true with reference to formic, oxalic, and gallic acids. These acids, formerly secured almost entirely from Germany, are now being made in the United States in substantial amounts.

The dye plant of the National Aniline and Chemical Co., located on Jamaica Bay, Brooklyn, N. Y., has been transferred to a new corporation, and will hereafter be known as the Hilwalkal Corporation. This property was formerly the plant of the W. Becker Aniline and Dye Works, and the Beckers Company.

The Atlantic Dyestuffs Company has purchased the L. H. Shattuck Company's shipyard at Portsmouth, N. H., and also considerable of the equipment and material that was in the yard, and will use the site for a plant for the manufacture of dyes. The yard comprises twelve shipways and covers about 100 acres, with a waterfront of about 2,000 ft. along the Piscataqua River, four and a half miles upstream from Portsmouth, N. H.

The General Chemical Co., New York, has purchased the Western Chemical Co., of Denver, Colorado. The capitalization of the Western Chemical Company is $2,000,000.

The experimental paper mill of Arthur D. Little, Inc., Cambridge, Mass., is working on the commercial production of acid-washed filter paper for quantitative chemical analysis, which was formerly imported. The mill will be able to meet the entire American demand with the highest quality product. For some time the mill has been demonstrating the paper-making quality of linters and cotton hull fiber which were used for smokeless powder during the war.

The suit in the U. S. District Court against the Cassett Bros. Company to enjoin them from selling salvarsan, brought by the Chemical Foundation, Inc., the Dermatological Research Laboratories, the Takamine Laboratories, the Diarsenol Company, and the H. A. Metz Laboratories, is to be dropped on the understanding that the Cassett Bros. Company will discontinue the sale.

The Butterworth-Judson Corporation announces that it has under construction new plants for the production of Gamma acid, H acid and J acid, and that preparations are being made to market a great many colors of this line as soon as the intermediate plants have been completed. The research department has also been doing considerable work on cyanthrol.

The War Trade Board Section of the Department of State has announced that general import license PBF No. 37, War Trade Board Ruling 837, issued December 1, 1919, has been revised and extended, effective January 10, 1920, so as to permit the importation thereunder without individual import licenses, of salvarsan, neosalvarsan, arsphenamine and all substitutes therefor and equivalents thereof, and narcotics, from all countries, excepting those parts of Russia under control of the Bolshevik authorities. The War Trade Board Section has extended to February 15, 1920, the time during which applications for Allocation Certificates allowing the importation of German dyes will be considered.

The Marentay Varnish Company has been organized at Detroit, Mich., with $150,000 capital, to manufacture and sell varnishes, chemicals, and paints.

The Sherwin-Williams Company have moved their general sales and executive departments from 116 West 32d Street to larger quarters at 115 Broadway, New York City.

The Northwestern Turpentine Company is to extract rosin by a new process from a tract of Douglas fir timber of 160 acres, near Disston, Oregon.

The Chemical Foundation, Inc., has recently issued two pamphlets, one describing the present status of vat dye patents held by the Foundation, the other covering metallurgical patents. These pamphlets may be secured at a price of 30 cents each by addressing the Chemical Foundation, Inc., 81 Fulton St., New York City.

The General Chemical Co., 25 Broad St., New York, and the Solvay Process Co., of Syracuse, N. Y., have organized the Atmospheric Nitrogen Corporation, for the development of nitrogen fixation, with $5,000,000 capital. According to R. L. Pierce, president of the Solvay Process Co., it is contemplated to erect a development plant at Syracuse, N. Y., at an approximate cost of $1,000,000. The following officers have been elected: E. L. Pierce, president; A. W. Hudson, treasurer; Ernest Jones, secretary; directors — Mr. Pierce, H. H. S. Handy, E. L. Miller, W. H. Nichols, Jr., Henry Wigglesworth, and Harold Otis.

The Shipping Board has invited proposals to furnish 18,900,000 to 28,000,000 barrels of fuel oil at domestic ports for the year beginning April 1920. This is twice the amount consumed during 1919. Bids will close February 9, 1920.

PERSONAL NOTES

Dr. R. C. Maclaurin, president of the Massachusetts Institute of Technology since 1908, an eminent scientist, lawyer, and executive, died at his home in Cambridge, Mass., January 15, of pneumonia.

Mr. Oscar Evard Collenberg, docent in the University of Upsala, has been elected as successor to the late Professor Farup in the Norges Techniske Höiskole.

According to a recent announcement, the following changes have been made in the personnel of the chemical laboratory at Frankford Arsenal: **Mr. Louis Hendler** has been promoted to the position of chief chemist-in-charge of the chemical research work; **Mr. George A. Miller, Jr.**, has been appointed metallurgist-in-charge of the metallurgical work, and **Mr. H. C. Pritham**, who was formerly with the explosives section of the Ordnance Department at Washington, D. C., has been retained as explosives chemist-in-charge of explosives and primer investigation.

Mr. George D. McLaughlin has resigned his position as chief chemist of Kullman, Salz & Co., tanners, of Benicia and San Francisco, Calif., to do research work in colloid chemistry, under Dr. Martin H. Fischer, at the University of Cincinnati, Cincinnati, Ohio.

Mr. Paul O. Powers, formerly with the Atlantic Dyestuff Co. of Burrage, Mass., where he was employed after being discharged from the Chemical Warfare Service, is now in the azo department of the U. S. Color and Chemical Co., of Ashland, Mass.

Mr. R. E. Andrew, formerly First Lieutenant in the Sanitary Corps, food and nutrition section, U. S. A., A. E. F., recently joined the staff of the Connecticut Agricultural Experiment Station, New Haven, Conn., as assistant chemist in the food and drug laboratory.

Mr. Charles H. Chandler has accepted the position of special investigational chemist for the Preston and Banes Bay Divisions of the United Fruit Company, in connection with their cane sugar factories and plantations. Mr. Chandler is located at Preston, Oriente, Cuba.

According to a recent announcement in the *New York Commercial*, **Mr. A. H. Jacoby** has been appointed, at the instance of officials in the War Trade Board Section of the State Department, as technical adviser on dyes and pharmaceutical chemicals to the organization committee of the Reparations Committee at Paris. Mr. Jacoby will sail at once and remain abroad for about three months. He will represent this country in the distribution of the German dyes to be allocated to the United States.

Mr. A. A. Bissiri, formerly in the research department of Parke, Davis & Co., Detroit, Mich., has accepted the position of superintendent of the Guasti Chemical Co., Los Angeles, Cal.

Dr. Arthur R. Hitch, formerly chief chemist for the Ashland Iron and Mining Co., Ashland, Ky., is now research chemist with the E. I. du Pont de Nemours & Co., at their Jackson Laboratories, Wilmington, Del.

Drs. E. V. McCollum, L. B. Mendel, John R. Murlin, Alonzo Taylor, Geo. H. A. Clowes, Lawrence J. Henderson, S. C. Prescott, W. D. Bancroft, and **C. E. Mendenhall** have been appointed by the National Research Council as members of an Advisory Board for the American Institute of Baking at Minneapolis, Minn. It will be the purpose of this Board to advise and direct the problems of the Institute and to work with it in solving the fundamental problems which are concerned with baking fermentology, and with the production of bread that satisfies every need of human nutrition.

Mr. James G. Vail, chemical director of the Philadelphia Quartz Co., has been called to Europe under the direction of Mr. Herbert Hoover to assist in the distribution of food supplied by the Allied Relief Association European Children's Fund. He sailed for Germany last November and plans to be gone until the harvest of the 1920 German crops, returning to his duties with Philadelphia Quartz Co., probably in August 1920.

Mr. Lawrence R. Taylor and **Mr. Harry E. Bishop** have resigned from the staff of the State Board of Health Laboratories at Indianapolis, Indiana. Mr. Taylor has accepted the position as director of scientific work for the French Lick Springs Hotel Co., French Lick, Ind., while Mr. Bishop will do special research work in the laboratory of the National Association of the Manufacturers of Glass Containers, at Chicago.

A Chemists' Club has been organized by the members of the Chicago Section of the American Chemical Society for the purpose of having a place for chemists where science is not the only topic discussed and where they can get together for friendly visits, and where chemists from other cities can be entertained. The following officers have been elected: Wm. Hoskins, president; Frank M. DeBeers, first vice president; W. Lee Lewis, second vice president; Chas. C. Kawin, treasurer; and Paul Van Cleef, secretary. Trustees elected are as follows: H. O. Baker, E. F. Buchanan, R. E. Doolittle, Otto Eisenschiml, L. V. Redman, and F. W. Willard. The headquarters of the Club are at 315 Plymouth Court, Chicago.

According to a recent announcement the chemists and engineers of Savannah, Ga., have organized a Chemists' and Engineers' Club, with headquarters at 23 East Gordon St., Savannah. The officers of this club are as follows: Mr. J. H. Allen, president; Dr. V. H. Bassett, vice president; Mr. Baldwin Bridger, secretary, and Mr. P. McG. Shuey, treasurer. This club gives a cordial welcome to all visiting chemists, engineers, and technical men.

Dr. C. von Egloffstein, expert food chemist and pioneer in the malt extract business, passed away December 5, 1919, after a prolonged illness. Dr. von Egloffstein was for the past twelve years in the employ of the American Diamalt Co., of Cincinnati, Ohio. Previous to 1907, he was with the Malt Diastase Co., of Brooklyn, N. Y., and from 1887 to 1897 he was with the Maltine Mfg. Co., of Brooklyn. Dr. von Egloffstein was always a very interested member of the Society, being a member of the New York Section from 1890 to 1907, when he transferred to the Cincinnati Section.

Mr. William L. Long recently left the employ of Swan-Myers, of Indianapolis, Ind., where he was employed as bacteriologist, and has secured a position as chemist with the H. K. Mulford Co., of Philadelphia, Pa.

Dr. Charles S. Palmer, formerly of the Mellon Institute, Pittsburgh, has joined the United Fuel Gas Co., Charleston, W. Va., as chief chemist.

Mr. John G. McLeod, Jr., has become research chemist in the Technical Service Department of the Brompton Pulp and Paper Co., Ltd., East Angus, Quebec, Canada.

Prof. Herbert Spencer Woods, assistant in the department of physiology, pharmacology and biochemistry of Baylor University, College of Medicine, Dallas, Texas, died January 4, 1919, following an operation. Professor Woods received the A.B. and A.M. degrees at the University of Missouri. He will be remembered for work done with the late Waldemar Koch on the quantitative estimation of the lecithins and other work done at various agricultural experiment stations of the United States.

Mr. J. E. Toomer, formerly research chemist with the Chino Copper Co., Hurley, N. M., has accepted a position as chief chemist with the Morris Fertilizer Co., Atlanta, Georgia.

Mr. C. Luther Masser has resigned as instructor of chemistry at Philadelphia Textile School, Philadelphia, Pa., to accept a position as supervising chemist with the New York Quinine and Chemical Works, Brooklyn, N. Y.

Capt. W. E. Brophy, formerly of the Barrett Co., and later of the Chemical Warfare Service, U. S. A., **Lieut. Robert F. LaBarron**, formerly of the U. S. Field Artillery, and **Mr. Chester G. Gilbert**, economic geologist and mining engineer, formerly of the Smithsonian Institution, have joined the engineering staff of Arthur D. Little, Inc., Cambridge, Mass.

Mr. E. H. Leslie has resigned his position as assistant to the vice president and general manager of the U. S. Industrial Alcohol Co., New York, N. Y., and has accepted a position as associate professor of chemical engineering in the University of Michigan, Ann Arbor, Michigan.

Mr. H. P. Zeller, formerly superintendent of the By-Product Coke Plant, of the Toledo Furnace Co., Toledo, Ohio, and later working in the Ordnance Department on the production of toluol, has for the past year been vice president and general manager of the Donner Union Coke Corp., Buffalo, N. Y.

Dr. Allerton S. Cushman will deliver the 1920 course under the Westbrook Foundation at the Wagner Free Institute of Science in Philadelphia. The lectures, four in number, on "Chemistry and Civilization," will be on successive Saturday evenings, beginning early in March. The lectures are freely open to the public.

GOVERNMENT PUBLICATIONS

By R. S. McBride, Bureau of Standards, Washington

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

GEOLOGICAL SURVEY

Gradations from Continental to Marine Conditions of Deposition in Central Montana during the Eagle and Judith River Epochs. C. F. Bowen. Professional Paper 125-B. Shorter contributions to General Geology, 1919. 11 pp. Issued October 20, 1919.

Geology and Ground Waters of the Western Part of San Diego County, California. A. J. Ellis and C. H. Lee. Water Supply Paper 446. 321 pp. Paper, $1.00. This was prepared in coöperation with the Department of Engineering of the State of California and the City of San Diego.

Slate in 1918. G. F. Loughlin and A. T. Coons. Separate from Mineral Resources of the United States, 1918, Part II. 16 pp. Issued October 23, 1919.

The value of the slate sold by the slate quarrymen of the United States in 1918 was $4,038,770. This shows a decrease of 30 per cent ($1,711,196) from the value for 1917. The total values for these two years cannot reasonably be compared, as the figures for 1918 do not include a considerable value of output for slate granules for patent roofing, which was used in large quantities in the construction of the government and other buildings necessitated by the war. Figures of slate granule production in 1918 are withheld so as not to disclose confidential information. The only slate product that showed increase in value in 1918 was mill stock, although the quantity sold showed a decrease.

Antimony in 1918. H. G. Ferguson. Separate from Mineral Resources of the United States, 1918, Part I. 25 pp. Issued October 18, 1919.

The United States is dependent upon three classes of material as sources of antimony or its alloys or compounds. (1) Antimony ore is imported from China (direct or via Japan), Bolivia (via Chile and Peru), and Mexico, and small quantities of ore are produced in the western United States. (2) Liquated antimony sulfide, also known as "crude antimony," "needle antimony," and antimony matte, is imported in small quantity from China. This material is produced by submitting the ores of the natural antimony sulfide, stibnite, to a red heat sufficient to melt but not to decompose it, and the metallic sulfide is then run into molds and allowed to cool. (3) Metallic antimony, known as antimony regulus, is imported from China, Japan, and Mexico, and during the war was produced in small quantity in the United States from both foreign and domestic ores. The metallic antimony imported from Japan is derived mainly from the refining of Chinese ore or "crude." A fourth class of material which should also be mentioned is antimonial lead, carrying from 12 to 18 per cent of antimony. Any of the three classes of materials noted above may enter into this product, but it is derived mainly from lead ores, most of them of the antimonial variety.

Domestic producers could not make a profit at the prices prevailing in 1918 and only about 190 tons of ore, containing about 50 tons of antimony, were mined. The antimony smelters continued production from imported ores until November, when all production of metallic antimony was temporarily suspended.

Most of the producers of antimony ore report that a price of 20 to 25 cents a pound for metal would be required to give ore prices sufficient to make the mining of domestic antimony ore profitable at the cost prevailing in 1918. It is probable, however, that antimony mining could be undertaken if there was assurance that a price of 16 or 17 cents would be continued over a considerable period, and according to one operator assurance of a steady price of 11 or 12 cents a pound would encourage production.

There is no reason to expect that prices of antimony will increase greatly during 1919, unless there should be a greatly increased tariff on antimony and antimony ores, as a surplus of antimony seems to be the condition over the entire world.

Antimony Ore Produced in the United States, 1915–1918

Year	Ore (Short tons)	Metal Content (Short tons)
1915	5,000	2,100
1916	4,500	1,770
1917	1,060	390
1918	190	50

Metallic Antimony Produced at Smelters in the United States 1917 and 1918

Year	From Domestic Ores (Short tons)	From Foreign Ores (Short tons)
1917	258	2,182
1918	127	2,490

By-Product Antimonial Lead Produced in the United States from Both Foreign and Domestic Ores, 1916–1918

Year	Gross Weight (Short tons)	Antimony Content (Short tons)	Value of Antimony Contents[1]
1916	24,038	3,496	$1,775,968
1917	18,646	2,759	1,142,226
1918	18,570	2,566	646,632

[1] Calculated on basis of average yearly price of 25.4 cents a pound, or $508 a short ton, in 1916, of 20.7 cents a pound, or $414 a short ton, in 1917, and of 12.6 cents a pound, or $252 a short ton, in 1918, for ordinary grades in the New York market.

Antimony Content of Secondary Alloys Recovered from Old Alloys, Scrap, and Dross, 1913–1918

Year	Quantity (Short tons)	Value[1]
1913	2,705	$401,963
1914	2,646	444,844
1915	3,102	1,811,568
1916	4,480	2,270,016
1917	4,961	2,061,700
1918	5,183	1,306,116

[1] Values calculated at average yearly price for ordinary brands of antimony as published by the *American Metal Market*.

Fuller's Earth in 1918. J. Middleton. Separate from Mineral Resources of the United States, 1918, Part II. 6 pp. Issued August 27, 1919.

There was a remarkable activity in the fullers' earth industry in 1918. Domestic fuller's earth is used chiefly in refining petroleum, and, as a result of the increase in the production of petroleum, the quantity, value, and average price per ton of fuller's earth sold in 1918 were by far the largest ever recorded by the United States Geological Survey, the increase in quantity being 11,901 short tons, or 16 per cent, and in value $374,267, or 48 per cent, compared with 1917. Although the demand was good, the conditions of labor, fuel, and transportation tended to restrict the output. The imports, on the other hand, on account of the scarcity of bottoms and of the increase in ocean freights, declined 4,387 tons, or 26 per cent. The value of imported fuller's earth (reported as at the foreign port of shipment) decreased $10,882, or 6 per cent. The apparent consumption—production plus imports—increased from 89,561 short tons in 1917 to 97,075 tons in 1918, an increase of 7,514 tons, or 8 per cent. On this basis the domestic production formed 87 per cent of the consumption in 1918, against 81 per per cent in 1917. Exports of fuller's earth, if any, were not separately classified.

Deposits of Manganese Ore in New Mexico. E. J. JONES. Bulletin 710-B. Contributions to Economic Geology, 1919, Part I. 24 pp. Issued October 21, 1919.

The total production in New Mexico of ores containing 35 per cent or more of manganese to December 31, 1918, was approximately 5,500 tons. A few deposits in the state are capable of yielding several thousand tons each of high-grade ore, but most of the deposits are small, containing from a few tons to several hundred tons each of high-grade ore. In view of the scanty developments on most of the deposits a close estimate of the ore reserves is not possible. The ores were shipped to furnaces in Chicago and other furnaces east of the Mississippi River. The minimum freight rate to Chicago is about $8 a long ton; the charges for mining and wagon transportation are high, and even at the high prices for manganese ores that prevailed during the summer of 1918 little profit was made.

BUREAU OF STANDARDS

A Comparison of the Heat Insulating Properties of Some of the Materials Used in Fire-Resistive Construction. W. A. HULL. Technologic Paper 130. 40 pp. Paper, 10 cents. Issued November 12, 1919.

An Apparatus for Measuring the Relative Wear of Sole Leathers, and the Results Obtained with Leather from Different Parts of a Hide. R. W. HART AND R. C. BOWKER. Technologic Paper 147. 10 pp. Paper, 5 cents. Issued November 22, 1918.

Location of Flaws in Rifle-Barrel Steel by Magnetic Analysis. R. L. SANFORD AND W. B. KOUWENHOVEN. Scientific Paper 343. 12 pp. Paper, 5 cents. Issued October 3, 1919.

COMMERCE REPORTS—DECEMBER 1919

Arrangements have been made in England for the distribution of the **dyestuffs and chemical drugs** to be furnished by Germany in accordance with the Peace Treaty. (P. 1219)

A plan has been proposed in England for charging consumers of **gas** for heat units furnished as computed from the volume of gas delivered, and its average calorific value. (P. 1333)

Government ownership of all the larger **electrical power plants** and transmission lines is being considered in Germany. (P. 1369)

The location and character of a large number of **chrome ore** mines in Asia Minor are described. (Pp. 1486–92)

The **nitrogen fixation** plants at Merseberg, Germany, are being enlarged to produce 300,000 tons of fixed nitrogen annually. (P. 1507)

Three large modern **cement** plants are now in operation in India. (Pp. 1526–8)

Among the important materials for the **paint industry** produced in Ireland are linseed oil, barytes, ochers, umbers, red oxide (obtained from iron sulfate produced by the oxidation of pyritiferous shales), white lead, zinc white, gypsum, and whiting. (Pp. 1570–2)

The indications are that the use of **fuel oil** will be greatly increased by Great Britain, especially for vessels. Efforts are being made to increase the **oil** output of the British Empire, especially in India, Trinidad, Egypt. and Canada. At present the British Empire furnishes only 2.5 per cent of the world's petroleum. (Pp. 1572, 1751–9)

Owing to the shortage of **petroleum** in Siberia, many substitutes are being used, such as wood distillation products for lighting, and coal tar for fuel. (P. 1581)

Among the **key industries** listed in the proposed Import and Export Regulation Bill in Great Britain, and for which importation will be permitted only under license, are: Coal-tar dyes and intermediates, synthetic drugs, chemicals and perfumes, analytical reagents and fine chemicals, optical glass, scientific glassware, illuminating glassware, laboratory porcelain, scientific and optical instruments, potassium compounds, tungsten and its alloys, zinc oxide and lithopone, arc lamp carbons and electrodes, magnetos and magnets, and gauges. (Pp. 1633–8)

A description is given of the **tungsten industry** of China. At present there is almost complete stagnation, due to reduced demands since the armistice. (P. 1657)

In a review of the **oil and fat industry** of Germany, it is pointed out that large importations will be necessary. Germany will prefer to import raw materials and press the oil in Germany; but there will be increased difficulty in obtaining foreign raw materials, due to the increased development of the oil milling industry in other countries, especially Japan and the United States. Efforts to obtain oil substitutes for the manufacture of soap, candles, and linoleum have not been successful. (Pp. 1687–9)

The **vegetable oil industry** of the Netherlands is described in detail. The oils produced are used largely in the margarine industry, the linseed oil in the paint and varnish industry, and other oils in soaps, candles, etc. The oil cake is used as cattle food in dairy farming. The principal oil seeds imported are almonds, copra, linseed, palm nuts, rape seed, peanuts, and soy beans. (Pp. 1780–91)

SPECIAL SUPPLEMENTS ISSUED DURING THE MONTH

FRANCE—5*b* and *c*
ITALY—8*c*
NORWAY—10*b*
SPAIN—15*f*
UNITED KINGDOM—19*g* and *h*
CANADA—23*b*
GUIANA—44*c*
JAPAN—55*a*

STATISTICS OF EXPORTS TO THE UNITED STATES

HANKOW, CHINA—(P. 1514)
Antimony
Egg albumin
Gall nuts
Hides
Soy bean oil
Cottonseed oil
Sesame seed oil
Tea oil
Wood oil
Nut oil
Potassium sulfate
Rhubarb
Tallow

FRANCE—Sup. 5*b* and 5*c*
Calcium tartrate
Glue
Hides
Essential oils
Paper
Photographic goods
Sodium formate
Copper matte
Artificial silk

BIRMINGHAM, ENGLAND—Sup. 19*b*
Precipitated chalk
Ammonium carbonate
Ammonium chloride
Sulfur
Sodium bicarbonate
Diamond dust
Gelatin
Glass
Glue
Iridium
Chrome yellow
Indian red
Varnish
Artificial silk
Silver-plated ware
Soap

ITALY—Sup. 8*c*
Citric acid
Cork
Essences
Licorice
Mannite
Olive oil
Hides
Sumac
Crude tartar
Glue
Graphite
Pumice
Talc

SPAIN—Sup. 15*f*
Garnets
Iron ore
Beeswax
Aconite
Ergot
Licorice
Calcium tartrate
Potash
Thymol
Gelatin
Glue
Hides
Olive oil
Red oxide of iron
Paper stock

BRITISH GUIANA—Sup. 44*c*
Balata
Bauxite
Coconut oil
Copra
Gold
Hides

JAPAN—Sup. 55*a*
Aluminum leaf
Antimony
Bronze
Celluloid
Agar-agar
Camphor
Caffeine
Cutch extract
Sodium cyanide
Dextrin
Gambier
Glycerin
Gum arabic
Gutta jelutong
Iodine
Menthol
Creosote oil
Fusel oil
Phosphorus
Potassium salts
Quinine
Licorice
Shellac
Sodium potassium (carbonate)
Sulfur
Paraffin wax
Vegetable wax
Zinc oxide
Copper
Graphite crucibles
Soap fats
Fertilizers
Glass
Gold leaf
Hides
Rubber
Iridium
Matches
Fish oil
Vegetable oils
Manganese ore
Molybdenum ore
Tungsten ore
Paper
Platinum
Graphite
Porcelain
Oil seeds
Tin
Zinc dust

NEW PUBLICATIONS

By Clara M. Guppy, Librarian, Mellon Institute of Industrial Research, Pittsburgh

Boiler Feed Water: A Concise Handbook of Water for Boiler Feeding Purposes. P. G. Jackson. 12mo. 102 pp. Price, $2.00. J. B. Lippincott Co., Philadelphia.

Carbohydrates: The Simple Carbohydrates and the Glucosides. E. F. Armstrong. 3rd Ed. 8vo. 239 pp. Price, $4.00. Longmans, Green & Co., New York.

Catalysis in Industrial Chemistry. G. G. Henderson. 202 pp. Price, $3.00. Longmans, Green & Co., New York.

Chemical Industries of France: L'Essor des Industries Chimiques en France. Ressources et Avenir de ces Industries. Eugène Grandmougin. 2nd Ed. Revised and Enlarged. 328 pp. Price, 16 fr.50. H. Dunod, Paris

Chemistry: Cours de Chimie. R. DeForcrand. 2 Vol. 2nd Ed. 8vo. Price, Vol. 1, 14 fr. Vol. 2, 18 fr. Gauthier-Villars et Cie, Paris.

Chemistry: Creative Chemistry; Descriptive of Recent Achievements in the Chemical Industries. E. E. Slosson. 8vo. 311 pp. Price, $2.50. Century Co., New York.

Chemistry: Handbook of Chemistry and Physics. Hodgman, Coolbaugh, and Senseman. 7th Ed. 533 pp. Price, $2.50. Chemical Rubber Co., Cleveland, Ohio.

Chemistry from the Industrial Standpoint. P. C. Thorne. 8vo. 260 pp. Price, 4s. 6d. Hodder & Stoughton, London.

Colloidal Chemistry and Its General and Industrial Applications. 2nd Report. British Association for the Advancement of Science. 172 pp. Price, 1s. 6d. British Association for the Advancement of Science, London.

Enzyme Action, Nature of. W. M. Bayliss. 4th Ed. 8vo 190 pp. Price, $2.50. Longmans, Green & Co., New York.

Explosives: Manufacture and Testing of Military Explosives. J. A. Marshall. 8vo. 257 pp. Price, $3.00. McGraw-Hill Book Co., New York.

Heat and Heat Engines, Text-Book of. Andrew Jamieson. 18th Ed. Revised by E. S. Andrews. 12mo. Vol. 1. 551 pp. Price, $3.00. J. B. Lippincott Co., Philadelphia.

Industrial Research, Outlook for Research and Invention. N. M. Hopkins. 256 pp. Price, $2.00. D. Van Nostrand Co., New York.

Leather Chemistry: Practical Leather Chemistry; A Handbook of Laboratory Notes and Methods for the Use of Students and Works Chemists. Arthur Harvey. 8vo. 207 pp. Price, 15s. C. Lockwood & Son, London.

Metallography: Principles of Metallography. R. S. Williams. 8vo. 155 pp. Price, $2.00. McGraw-Hill Book Co , New York.

Mineral Industry, 1918. *Edited* by G. A. Roush. Vol. 27. 8vo. 937 pp. Price, $10.00. McGraw-Hill Book Co., New York.

Minerals and Ores of the Rarer Elements, Analysis of; For Analytical Chemists, Metallurgists and Advanced Students. W. R. Schoeller and A. R. Powell. 8vo. 239 pp. Price, $5.00. J. B. Lippincott & Co., Philadelphia.

Ore Analysis: Technical Methods of Ore Analysis. A. H. Low. 8th Ed. Revised and Enlarged. 8vo. 388 pp. Price, $3.25. John Wiley & Sons, Inc , New York.

Organic Chemistry: Handbuch der Organischen Chemie. F. K. Beilstein. 4th Ed. 982 pp. Price, $15.00. G. E. Stechert & Co., New York.

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MARKET REPORT—JANUARY, 1920

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

		Jan. 1	Jan. 15
Acid, Boric, cryst., bbls.	lb.	.14½	.14½
Hydrochloric, com'l, 22°	lb.	.02	.02
Hydriodic	oz.	.19	.19
Nitric, 40°	lb.	.07	.07
Phosphoric, 50% tech.	lb.	.24	.24
Sulfuric, C. P.	lb.	.08	.08
Chamber, 66°	ton	22.00	22.00
Oleum	ton	27.00	27.00
Alum, ammonia, lump	lb.	.04	.04
Aluminum Sulfate (iron-free)	lb.	.03	.03
Ammonium Carbonate, pwd.	lb.	.13	.13
Ammonium Chloride, gran.	lb.	.15	.15
Ammonia Water, carboys	lb.	.10½	.10½
Arsenic, white	lb.	.10½	.11
Barium Chloride	ton	95.00	95.00
Nitrate	lb.	.11	.11
Barytes, white	ton	25.00	25.00
Bleaching Powd., 35%, Works,	100 lbs.	2.50	2.75
Borax, cryst., bbls.	lb.	.09	.09
Bromine, tech., bulk	lb.	.60	.60
Calcium Chloride, fused	ton	21.00	21.00
Chalk, precipitated	lb.	.05½	.05½
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	8.00	8.00
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.50	1.50
Iodine, resublimed	lb.	4.10	4.10
Lead Acetate, white crystals	lb.	.14	.14
Nitrate	lb.	.15	.15
Red American	100 lbs.	.10½	.10½
White American	100 lbs.	.09½	.09½
Lime Acetate	100 lbs.	2.00	2.00
Lithium Carbonate	lb.	1.50	1.50
Magnesium Carbonate, powd.	lb.	.19	.19
Magnesite	ton	65.00	65.00
Mercury flask	75 lbs.	85.00	93.00
Phosphorus, yellow	lb.	.35	.35
Plaster of Paris	100 lbs.	1.50	1.50
Potassium Bichromate	lb.	.30	.28
Bromide	lb.	.85	.85
Carbonate, calc., 80–85%	lb.	.24	.24
Chlorate, cryst.	lb.	.18	.15
Cyanide, bulk, 98–99%	lb.	.30	.30
Hydroxide, 88–92%	lb.	.28	.28
Iodide, bulk	lb.	3.35	3.35
Nitrate	lb.	.14	.14
Permanganate, U. S. P.	lb.	.60	.70
Salt Cake	ton	17.00	17.00
Silver Nitrate	oz.	.81½	.82½
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	2.25	2.25
Caustic, 76%	100 lbs.	4.25	4.25
Sodium Acetate	lb.	.25	.25
Bicarbonate	100 lbs.	2.25	2.25
Bichromate	lb.	.22	.18
Chlorate	lb.	.15	.12
Cyanide	lb.	.30	.30
Fluoride, technical	lb.	.15	.15
Hyposulfite	100 lbs.	3.60	3.60
Nitrate, 95%	100 lbs.	3.25	3.35
Silicate, 40°	lb.	.02	.02
Sulfide	lb.	.05	.05
Bisulfite, powdered	lb.	.05	.05
Strontium Nitrate	lb.	.23	.23
Sulfur, flowers	100 lbs.	3.75	3.75
Crude	long ton	30.00	30.00
Talc, American, white	ton	20.00	20.00
Tin Bichloride	lb.	.21½	.21½
Oxide	lb.	.60	.60
Zinc Chloride, U. S. P.	lb	.22	.22
Oxide	lb.	.60	.60

ORGANIC CHEMICALS

		Jan. 1	Jan. 15
Acetanilid	lb.	.55	.55
Acid, Acetic, 28 p. c.	lb.	.02½	.02½
Glacial	lb.	.12	.12
Acetylsalicylic	lb.	1.00	1.00
Benzoic, U. S. P., ex-toluol	lb.	.85	.85
Carbolic, cryst., U. S. P., drs.	lb.	.15	.15
50- to 110-lb. tins	lb.	.20	.20
Acid (*Concluded*)			
Citric, crystals, bbls.	lb.	.87	.84
Oxalic, cryst., bbls.	lb.	.32	.35
Pyrogallic, resublimed	lb.	2.50	2.50
Salicylic, bulk, U. S. P.	lb.	.55	.55
Tartaric, crystals, U. S. P.	lb.	.70	.67
Trichloracetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.14	.14
Alcohol, denatured, 190 proof	gal.	.75	.78
Ethyl, 190 proof	gal.	4.75	5.25
Wood, 95%	gal.	1.75	2.00
Amyl Acetate	gal.	3.65	3.65
Camphor	lb.	3.50	3.40
Carbon Bisulfide	lb.	.08	.08
Tetrachloride	lb.	.11	.11
Chloroform, U. S. P.	lb.	.30	.30
Creosote, U. S. P.	lb.	1.15	1.00
Cresol, U. S. P.	lb.	.17	.17
Dextrine, corn	lb.	.07	.07
Imported Potato	lb.	.17	.17
Ether, U. S. P., conc., 100 lbs.	lb.	.17	.19
Formaldehyde	lb.	.35	.50
Glycerin, dynamite, drums	lb.	.24	.25
Starch, corn	100 lbs.	5.35	5.35
Potato, Jap.	lb.	.07½	.07½
Rice	lb.	.25	.25
Sago	lb.	.05	.05

OILS, WAXES, ETC.

		Jan. 1	Jan. 15
Beeswax, pure, white	lb.	.65	.65
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	.19	.18
Ceresin, yellow	lb.	.14	.14
Corn Oil, crude	lb.	.19	.19
Cottonseed Oil, crude, f. o. b. mill	lb.	.19½	.19½
Menhaden Oil, crude (southern)	gal.	.95	.95
Neat's-foot Oil, 20°	gal.	2.25	2.25
Paraffin, 128–130 m. p., ref.	lb.	.10½	.10½
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs.	bbl.	18.25	18.25
Rosin Oil, first run	lb.	.97	.97
Shellac, T. N.	lb.	1.30	1.70
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.95	1.95
Stearic Acid, double-pressed	lb.	.26	.27
Tallow Oil, acidless	gal.	1.50	1.55
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	1.80	1.97

METALS

		Jan. 1	Jan. 15
Aluminum, No. 1, ingots	lb.	.32½	.32
Antimony, ordinary	100 lbs.	9.87	9.87
Bismuth	lb.	2.70	2.52
Copper, electrolytic	lb.	.21½	.19
Lake	lb.	.22	.19½
Lead, N. Y.	lb.	.09	.09
Nickel, electrolytic	lb.	.45	.45
Platinum, refined, soft	oz.	160.00	160.00
Silver	oz.	1.32	1.36
Tin	lb.	.62½	.62½
Tungsten Wolframite	per unit	7.00	7.00
Zinc, N. Y.	100 lbs.	8.75	9.75

FERTILIZER MATERIALS

		Jan. 1	Jan. 15
Ammonium Sulfate	100 lbs.	7.00	7.00
Blood, dried, f. o. b. N. Y.	unit	7.50	7.50
Bone, 3 and 50, ground, raw	ton	48.00	48.00
Calcium Cyanamide, unit of Ammonia		4.50	4.50
Fish Scrap, domestic, dried, f. o. b. works	unit	7.25	7.25
Phosphate Rock, f. o. b. mine:			
Florida pebble, 68%	ton	Nom.	Nom.
Tennessee, 78–80%	ton	11.00	11.00
Potassium muriate, 80%	ton	240.00	240.00
Pyrites, furnace size, imported	unit	.18	.18
Tankage, high-grade, f. o. b. Chicago	unit	7.50	7.50

COAL-TAR CHEMICALS

	Jan. 1	Jan. 15
Crudes		
Benzol, C. P. . . . . gal.	.27	.27
Cresol, U. S. P. . . . . lb.	.17	.17
Naphthalene, flake . . . . . lb.	.08	.08
Phenol . . . . . lb.	.15	.15
Toluol, 90% . . . . . gal.	.28	.28
Xylol, water white . . . . . gal.	.40	.48
Intermediates		
Acids:		
Benzoic . . . . . lb.	.80	.80
Broenner's . . . . . lb.	1.75	1.75
Cleves . . . . . lb.	2.00	2.00
Cresylic, 95% . . . . . lb.	.75	.75
Gamma . . . . . lb.	2.50	2.50
H . . . . . lb.	1.70	1.70
Metanilic . . . . . lb.	1.60	1.60
Monosulfonic . . . . . lb.	.15	.15
Napthionic, crude . . . . . lb.	.65	.65
Neville & Winther's . . . . . lb.	1.70	1.70
Sulfanilic . . . . . lb.	.35	.35
Amido Azo Benzol . . . . . lb.	1.15	1.15
Aniline Oil . . . . . lb.	.33	.35
For Red . . . . . lb.	.65	.65
Aniline Salt . . . . . lb.	.42	.42
Anthracene, 80% . . . . . lb.	.65	.65
Anthraquinone . . . . . lb.	5.50	5.50
Benzaldehyde, tech . . . . . lb.	.75	.75
U. S. P. . . . . . lb.	1.50	1.50
Benzidene Base . . . . . lb.	1.25	1.15
Benzidine Sulfate . . . . . lb.	1.00	.90
Diamidophenol . . . . . lb.	6.00	6.00
Dianisidine . . . . . lb.	10.00	10.00
p-Dichlorbenzol . . . . . lb.	.10	.10
Diethylaniline . . . . . lb.	1.40	1.40
Dimethylaniline . . . . . lb.	.90	.90
Dinitrobenzol . . . . . lb.	.26	.26
Dinitrotoluol . . . . . lb.	.38	.38
Diphenylamine . . . . . lb.	.65	.65
G Salt . . . . . lb.	.65	.65
Hydroquinone . . . . . lb.	2.00	2.00
Metol . . . . . lb.	11.50	11.50
Monochlorbenzol . . . . . lb.	.09	.09
Monoethylaniline . . . . . lb.	2.15	2.15
a-Naphthylamine . . . . . lb.	.33	.33
b-Naphthylamine . . . . . lb.	1.15	1.15
b-Naphthol, crude . . . . . lb.	.55	.55
m-Nitraniline . . . . . lb.	.95	.95
p-Nitraniline . . . . . lb.	1.20	1.25
p-Nitrobenzol, crude . . . . . lb.	.16	.16
Rectified (Oil Myrbane) . . . . . lb.	.18	.18
p-Nitrophenol . . . . . lb.	.80	.80
p-Nitrosodimethylaniline . . . . . lb.	.80	.80
o-Nitrotoluol . . . . . lb.	.17	.17
p-Nitrotoluol . . . . . lb.	1.15	1.15
m-Phenylenediamine . . . . . lb.	1.10	1.10
p-Phenylenediamine . . . . . lb.	2.40	2.25
Phthalic Anhydride . . . . . lb.	.60	.60
Primuline Base . . . . . lb.	4.00	4.00
R Salt . . . . . lb.	.62½	.62½
Resorcin, tech . . . . . lb.	3.50	3.50
U. S. P. . . . . . lb.	6.00	6.00
Schaeffer Salt . . . . . lb.	.55	.55
Sodium Naphthionate . . . . . lb.	1.10	1.10
Thiocarbanilid . . . . . lb.	.60	.60
Tolidine, Base . . . . . lb.	1.65	1.65
Toluidine, mixed . . . . . lb.	.44	.44
o-Toluidine . . . . . lb.	.25	.25
m-Toluylenediamine . . . . . lb.	1.35	1.35
p-Toluidine . . . . . lb.	1.75	1.75
Xylidene, crude . . . . . lb.	.50	.50

COAL-TAR COLORS

	Jan. 1	Jan. 15
Acid Colors		
Black . . . . . lb.	1.15	1.15
Blue . . . . . lb.	3.00	3.00
Acid Colors (*Continued*)		
Fuchsin . . . . . lb.	2.50	2.50
Orange III . . . . . lb.	1.00	1.00
Red . . . . . lb.	1.10	1.10
Violet 10B . . . . . lb.	6.50	6.50
Alkali Blue, domestic . . . . . lb.	4.75	4.75
Imported . . . . . lb.	8.00	8.00
Azo Carmine . . . . . lb.	4.00	4.00
Azo Yellow . . . . . lb.	2.00	2.00
Erythrosine . . . . . lb.	12.00	12.00
Indigotine, conc . . . . . lb.	3.00	3.00
Paste . . . . . lb.	1.50	1.50
Naphthol Green . . . . . lb.	1.50	1.50
Ponceau . . . . . lb.	1.00	1.00
Scarlet 2R . . . . . lb.	1.00	1.00
Direct Colors		
Black . . . . . lb.	.95	.95
Blue . . . . . lb.	1.10	1.10
Brown . . . . . lb.	1.55	1.55
Fast Red . . . . . lb.	3.50	3.50
Yellow . . . . . lb.	2.00	2.00
Violet, con't . . . . . lb.	2.20	2.20
Chryosophenine, domestic . . . . . lb.	2.50	2.50
Imported . . . . . lb.	3.80	3.80
Congo Red, 4B Type . . . . . lb.	1.60	1.60
Primuline, domestic . . . . . lb.	3.00	3.00
Oil Colors		
Black . . . . . lb.	.70	.70
Blue . . . . . lb.	1.65	1.65
Orange . . . . . lb.	1.40	1.40
Red III . . . . . lb.	1.65	1.65
Scarlet . . . . . lb.	1.75	1.75
Yellow . . . . . lb.	1.70	1.70
Nigrosine Oil, solution . . . . . lb.	.90	.90
Sulfur Colors		
Black . . . . . lb.	.30	.30
Blue, domestic . . . . . lb.	.80	.80
Brown . . . . . lb.	.35	.35
Green . . . . . lb.	1.00	1.00
Yellow . . . . . lb.	.90	.90
Chrome Colors		
Alizarin Blue, bright . . . . . lb.	7.75	7.75
Alizarin Red, W. S. Paste . . . . . lb.	5.00	5.00
Alizarin Yellow R . . . . . lb.	1.50	1.50
Chrome Black, domestic . . . . . lb.	1.25	1.25
Imported . . . . . lb.	2.20	2.20
Chrome Blue . . . . . lb.	2.50	2.50
Chrome Green, domestic . . . . . lb.	1.50	1.50
Chrome Red . . . . . lb.	2.00	2.00
Basic Colors		
Auramine, O, domestic . . . . . lb.	2.25	2.25
Auromine, OO, imported . . . . . lb.	3.50	3.50
Bismarck Brown Y . . . . . lb.	.90	.90
Bismarck Brown R . . . . . lb.	1.20	1.20
Chrysoidine R . . . . . lb.	1.00	1.00
Chrysoidine Y . . . . . lb.	.90	.90
Green Crystals, Brilliant . . . . . lb.	6.00	6.00
Indigo, 20 p. c. paste . . . . . lb.	.75	.75
Fuchsine Crystals, domestic . . . . . lb.	4.00	4.00
Imported . . . . . lb.	12.00	12.00
Magenta Acid, domestic . . . . . lb.	4.25	4.25
Magenta Crystals, imported . . . . . lb.	10.00	10.00
Malachite Green, crystals . . . . . lb.	4.50	4.50
Methylene Blue, tech . . . . . lb.	2.25	2.25
Methyl Violet . . . . . lb.	2.60	2.60
Nigrosine, spts. sol . . . . . lb.	.85	.85
Water sol., blue . . . . . lb.	.65	.65
Jet . . . . . lb.	.90	.90
Phosphine G., domestic . . . . . lb.	7.00	7.00
Rhodamine B ex-con't . . . . . lb.	27.00	27.00
Victoria Blue, base, domestic . . . . . lb.	6.00	6.00
Victoria Green . . . . . lb.	6.00	6.00
Victoria Red . . . . . lb.	7.00	7.00
Victoria Yellow . . . . . lb.	7.00	7.00

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY
AT ESCHENBACH PRINTING COMPANY, EASTON, PA.

Volume XII MARCH 1, 1920 No. 3

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Published monthly. Subscription price to non-members of the American Chemical Society, $6.00 yearly; single copy, 60 cents
Price per single copy to American Chemical Society members, 50 cents. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted
Entered as Second-class Matter December 19, 1908, at the Post Office at Easton, Pa., under the Act of March 3, 1879
Acceptance for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized July 13, 1918

All communications should be sent to The Journal of Industrial and Engineering Chemistry
Telephone: Vanderbilt 1930 **Cable Address: Jiechem** **35 East 41st Street, New York City**
Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Secretary, 1709 G Street, N. W., Washington, D. C.

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EDITORIALS

DYES IN THE SENATE

One of the characteristics of the word "dye" is a begetfulness of unlimited oral expression. In the Senate the word naturally fell upon congenial soil. It was scarcely a matter of surprise, therefore, that on the single day, February 25th, set aside for the consideration of the Longworth Bill. prior to the reopening of the Peace Treaty discussion, no decisive vote should have been reached.

It had been hoped that in view of the unanimous report of the sub-Committee, followed by a similar unanimous support by the Finance Committee, the Senate might proceed to a quick passage of the bill. This hope was in vain.

The clear indication of the strength of those favoring the bill was given at the very outset when an effort to refuse to take up the bill commanded only 11 votes. The discussion was opened by a masterly presentation of the subject by Senator Watson, of Indiana, chairman of the sub-Committee. In spite of the technicalities of the subject Senator Watson showed how attentively he had listened to all of the testimony presented at the hearing. His plea for the speedy passage of the bill was straightforward and convincing. The many questions asked him by fellow Senators indicated the keen interest in the subject, though considerable doubt was created as to whether the questions by Senator Kenyon, of Iowa, were prompted by desire for knowledge or for the purpose of delay.

The treatment of the bill in the Senate was thoroughly non-partisan and it was particularly interesting to note the complete intermingling of Republican and Democratic Senators in the neighborhood of Senator Watson when he spoke.

One of the most perfect contributions of the day was the brief but eloquent speech of Senator Knox, of Pennsylvania, whose support of the measure as an important contribution to national security was unqualified.

Senator King, of Utah, surprised all by presenting the novel argument that it was unpatriotic of American manufacturers to ask for protection against the German dye interests and thereby cripple Germany in its effort to again get upon its feet.

More than an hour of the limited time available was lost through the efforts of Senator Poindexter, of Washington, to utilize the situation so as to force from the Finance Committee a report to the Senate of the bill protecting magnesite, which bill had been voted on favorably by the Committee but not ordered reported to the Senate.

At the conclusion of Senator Watson's speech adjournment was taken and according to the program previously announced by the leader of the Senate the Peace Treaty will now be continually before the Senate until it is disposed of. The Longworth bill, therefore, must wait. However, you never can tell. The unexpected may happen at any moment.

ST. LOUIS NEXT

At Buffalo there was the spirit of relaxation from the tension of war activities, at Philadelphia the proclamation of the chemical independence of America. What shall it be at St. Louis? The Spring Meeting of the SOCIETY, beginning April 12,1920, must have its distinctive mark. Plainly we should gather in a spirit of effective deliberation as to how we can best meet the increased responsibility which has been placed upon us by the American people. That such responsibility exists is evidenced by the sympathetic attitude of our representatives in Congress toward all legislation affecting the development of matters chemical.

It is no time to fold our hands in blissful contemplation of the felicitous consideration shown by our national legislative body, nor dare we content ourselves with group satisfaction over the increased popular appreciation of and regard for the work of the chemist. Pride goes before the fall!

On the contrary, it is just that time when chemists should meet together for common counsel and for cool-headed decision as to how best to justify the confidence and good-will which has been so ungrudgingly manifested. There must be no slackening of the pace, but rather a resolve to drive all the harder, driving, however, with that combination of caution and courage which will insure ultimate success.

It is fortunate that this meeting is to be held in St. Louis, that great city of the Middle West. The trend of war activities has naturally led to an abnormal stimulation of industrial chemistry in the states along the Atlantic seaboard, but such a one-sided development is unhealthy, it must be general in character and nation-wide in extent. Gatherings of the SOCIETY have always proved an effective stimulus. St. Louis, because of its strong position chemically, central location and ready accessibility, should draw a multitude of chemists. The New York Section has an active transportation committee already arranging for special cars to carry its members under most congenial conditions. Doubtless similar steps are being taken in other centers. The committees appointed by the St. Louis Section, and the presence of the University of Missouri Section as joint host, assure the successful handling of the meeting. Congratulations in advance on the policy of holding all meetings at headquarters, the Statler Hotel!

LOST GROUND TO BE RECOVERED

To day, March 1, is the date designated by the President for the return of the railroads to their owners. This act of restoration has been greeted by the nation with a profound feeling of satisfaction and relief. While fully recognizing the exigencies which made federal control necessary, nevertheless the brief experiment in government ownership has quite convinced our people that no more of it is wanted. One of the chief factors in the dissatisfaction with federal control has been the constantly recurring announcements of deficient income, and this means the taxpayer must make up the difference, running up to some $750,000,000.

That loss is perfectly apparent; there has, however, been another loss which unfortunately cannot be reckoned in dollars and cents with exactitude, but which we believe would also run into the millions if it could be so reckoned. This loss began when the Railroad Administration, among its very first acts, closed the research laboratories in which thorough chemical surveys of natural resources were being intelligently and enthusiastically carried on by various railway companies. This act was necessarily followed by the complete disintegration of the personnel of the laboratories and, it is to be feared, the loss of many records of valuable work already partially completed. To augment the destructive process the exhibition of natural resources by the railroads at the National Exposition of Chemical Industries was vetoed. To those who had watched from year to year the increasing value of these exhibits, this act seemed unaccountable, especially as Congress at the very time was drafting a bill appropriating millions of dollars for the development of sources of supply of certain minerals, and when it was universally recognized that the great war into which we had determined to throw every ounce of our energy was to be an undertaking which would call heavily on all the resources of the nation. Just at the time when the need was being recognized the Railroad Administration cut off the most logical means of filling it.

Appeals for a reversal of this most unfortunate policy were in vain, though it is understood that many in the Railroad Administration did not agree with the Director General in this matter; it was a day of autocratic power, however, and their voices could not be heard. Ample provision was made for lodging complaints as to the character of the service in the dining cars, but on the subject of chemical development of natural resources—nothing doing.

Well, the régime is ended and far-sighted business men are again in control. At the very outset they will have many vexing problems to solve, but there need be no delay in the rehabilitation of the chemical work, for the finances involved are trifling in amount.

Where shall the reinauguration begin? Naturally in the South, where the movement, prior to the war, had made its most effective advance. That section of our country which so often had accepted uncomplainingly the opprobrious epithet of unprogressiveness, outstripped the rest of the country in taking the chemist to itself as the surest means for transforming its undeveloped wealth into useful products. For this progressiveness two factors were chiefly responsible—first, the clear vision of the officers of the Carolina, Clinchfield and Ohio Railroad, which was the pioneer in this work and in making a resourceful chemist its chief industrial agent; second, the effective advocacy of this method of development by Mr. Richard H. Edmonds, the hard-hitting editor of *The Manufacturers Record*, whose vigorous editorials on the subject carried conviction among the thoughtful men of the South.

Call back your scattered chemists, Mr. Railroad President, reopen the laboratories, and provide even better facilities for carrying forward this great work which will yield rich returns in comparison with the small outlay of capital required.

Take up again, Mr. Edmonds, in this behalf your pen of power. You put this matter across once before, you can do it again.

Let the South again lead the way!

A LIFE OF SERVICE

Service—yes, and in that loftiest meaning of the word as it is used in Holy Writ—the service of mankind, so runs the record of Edgar Fahs Smith, whose resignation of both the Provostship and the Blanchard Professorship in the University of Pennsylvania has just been announced.

The announcement was startling in that it was unexpected; it was distressing because the act removes from our educational circles one who has always stood for sound scholarship and high ideals. His own intensive industry and happy disposition have constantly furnished a living example of the joy of work. Yet who would say him nay if he feels that the time has arrived when a change of work will enable him to continue better that outgiving of himself which has characterized his life?

To those who because of present injustices in the recompense of teachers are disposed to seek other lines of work there is a wealth of example in his forty-four years of service. To those who would commiserate the university executive because of the many perplexing and irritating problems so often presented, there is happy refutation in his statement, "My relations with everybody in the University for all these years have been of the most delightful nature." There is many a "Penn" alumnus who will reëcho that thought when he recalls some escapade which threatened separation from Alma Mater. Paradoxical as it may seem, he sought first the Provost for counsel, with certainty of common-sense justice and sympathetic fair-dealing.

That sympathy was not confined to the campus but was extended in our younger days to all of us who had chosen the calling of chemistry. The great ovation accorded Dr. Smith when he arose to address the AMERICAN CHEMICAL SOCIETY a year ago at Buffalo was a manifestation of the high regard in which he was held by his fellow chemists. None present could fail to note his deep emotion during President Nichols' introduction. He could not but feel the streams of love and loyalty pouring in on him from his audience in sympathetic response to the speaker's words.

Fortunately the present resignations are not indicative of any cessation of his fine activities, for he writes us in response to a request for details: "I am conscious that I have yet the power of doing a great deal of work. My health is in excellent condition. I am working hard at the present moment, and have been serving, in addition to my duties here, on the State Constitutional Commission and on other committees, so that probably I shall turn up somewhere else doing work. I can't be idle. It looks as if a change was the real need with me, and not a rest. I have not applied for any pension."

Whatever he may do, wherever he may go, Dr. Smith will always carry with him the best of good wishes from his fellow men.

INADEQUATE PATENT SERVICE

The United States Patent Office exists for the benefit of the citizens of this country; it was never intended to be a national dividend producer. Its work is carried on by appropriation from Congress; for the work done by its employees fees are charged from those who share its benefits. We are informed that during the life of the Patent Office the receipts to the Government from fees exceed the appropriations by approximately $7,000,000.

In spite of this remarkable showing, that important branch of government activity stands to-day handicapped in its efforts to give the best service to our citizens. Insufficient appropriations have made it impossible to retain an adequate experienced personnel or to attract those whose ability would insure best results, and have made necessary the curtailment of many lines of useful service which could and should be rendered.

A good illustration of the present inadequate service of the office is furnished in a case recently brought to our attention by a correspondent in Texas who desired photographic copies of foreign patents. Perhaps nowhere in this country except in the Patent Office in Washington can there be found complete files of foreign patents. In the past it has been the policy of the Office to furnish photographic copies of these foreign patents on payment of an appropriate fee. Within the last two months it has been found necessary, because of insufficient force and funds to discontinue this policy. This is extremely regrettable and is destined to prove a serious obstacle in the prosecution of research at points distant from Washington. The strength of our country lies in its bigness, but its size is also a weakness unless the difficulties of distance can be overcome. Our scientific workers are scattered in every state in the union. For the successful conduct of chemical work it is often necessary that copies of foreign patents be quickly secured.

We know the Commissioner of Patents too well to think for a moment that this change in policy has any other basis than the necessity of so administering the office that appropriations will not be exceeded. We appeal, therefore, to the members of the Patent Committee in Congress to provide the funds necessary for such strengthening and enlargement, of the personnel and the equipment of the Patent Office as will enable it to function effectively in all phases of its work, for citizens in all parts of the country. Inadequate service in the Patent Office at the present time will prove disastrous economy to the nation as a whole.

NOTES

What would have happened a few years ago to the scientist who might have had the boldness to predict that before long our Government would place a ban on exports of helium from this country? Nevertheless, such a prohibition has been recommended by the Navy Department.

The death of Professor Francis C. Phillips of Pittsburgh removes a well-known figure from the meetings of the Council and the SOCIETY. His heart's desire was the completion of the Priestley Memorial Fund. The successful prosecution of that work would now constitute a two-fold testimonial.

Chairman Angel of the National Research Council compresses a volume into a few words when he writes, in connection with the gift of $5,000,000 to the Council by the Carnegie Corporation, "It has taken the Council out of the range of purely promotional enterprises into one of a permanently established kind."

A wise first step has been taken in the utilization of Tech's $8,000,000 fund by an appropriation of $100,000 for immediate salary bonuses to all members of the instructing staff. Chemistry shows up strong in the personnel of the new Administrative Committee. Congratulations to Professors Talbot and Walker who constitute two-thirds of the faculty representation on the Committee.

The Federal Trade Commission has cited Shabakawa & Co., Inc., of New York City, for importing from Japan matches bearing the Swedish title, "Sakerhets Tandstickor," in prominent type, while the words "Made in Nippon" are printed so small as to be readily overlooked. We have heard that the wood for Swedish matches is shipped from Bayonne, N. J., and that the Japanese match machines are copies of those imported from America. Why not get rid of all of the complications by using American matches?

The Bureau of Vocational Information, 2 West 43rd St., New York City, has mailed an extended questionnaire to all of our women chemists. The function of this Bureau is to collect data concerning vocations for trained women and to conduct researches into opportunities and requirements in specific fields. Appropriate publicity will be given to the results of its researches. The work of the Bureau is in very capable hands, women of clear heads and far-sighted vision. It is fortunate for the woman chemist that such an organization is devoting an intensive study to chemistry as a profession for women. In true laboratory style it is first getting facts and the value of the deductions in the studies contemplated will depend primarily upon the completeness with which its questionnaire is answered. It would seem that no one should be unwilling to sacrifice the time necessary for the filling out and return of the questionnaire and we take pleasure in expressing the hope that the proportion of respondents will be 100 per cent.

CONTRIBUTIONS FROM THE CHEMICAL WARFARE SERVICE, U. S. A.

THE REMOVAL OF CARBON MONOXIDE FROM AIR[1]

By Arthur B. Lamb, William C. Bray and J. C. W. Frazer

Fixed Nitrogen Research Laboratory, American University, Washington, D. C.

Received January 16, 1920

The following article is a summary of investigations on the removal of carbon monoxide from air carried on at the American University Experiment Station[2] and at coöperating laboratories during 1917 and 1918. These investigations were supported mainly by funds allotted by the Navy Department, and led to the development and manufacture of a carbon monoxide mask for naval use.

CARBON MONOXIDE IN WAR—Carbon monoxide, because of its cheapness, accessibility, and ease of manufacture, has been frequently considered as a possible war gas. Actually, it appears never to have been used intentionally for such purposes. There are a number of reasons for this, but the decisive one certainly is its relatively slight toxicity. Several minutes' inhalation of a mixture of one part in 100 parts of air is required to produce unconsciousness, while with a number of other toxic gases actually employed, such as phosgene for instance, a similar length of exposure to one part in 100,000 parts of air, that is, to a mixture a thousand times more dilute, will prove fatal. Since it is very difficult to set up the required concentrations of even the most toxic gases over significant areas in the open, it is evident that no possible degree of cheapness, accessibility, etc., could overcome so serious a handicap.

Carbon monoxide is then quite out of the question for any *intentional* use as a toxic war gas, yet it is, nevertheless, a source of serious danger both in marine and land warfare, and defense against it has been found necessary. Defective ventilation in the boiler rooms of ships, and fires below decks both in and out of action, are specially dangerous because of the carbon monoxide which is produced. In one of the naval engagements between the Germans and the English, defective high explosive shells after penetrating into enclosed portions of ships, evolved large quantities of carbon monoxide, and this killed large numbers of the crew. On shore, machine gun fire in enclosed spaces such as pill boxes and in tanks liberates relatively large quantities of carbon monoxide and has been responsible for numerous casualties. Similarly in mining and sapping operations the carbon monoxide liberated from the detonation of high explosives constitutes one of the most serious of the difficulties connected with this work, and has necessitated elaborate equipment and extensive military training in mine rescue work.[1]

CARBON MONOXIDE IN PEACE—Carbon monoxide is also a serious hazard in peace as well as in war. In the manufacture of power and illuminating gas, and in the metallurgical industries where this gas is largely employed, casualties, and indeed fatalities, are constantly occurring. In coal mining, in certain classes of copper mining, and wherever explosives are used in confined spaces, carbon monoxide is a serious menace responsible for the loss of many lives each year. Leaky flues, exhaust gases from explosion engines, improper ventilation where coal fires are employed, and the air to which firemen are exposed in burning buildings, all constantly take a not inconsiderable toll of lives.

DIFFICULTY OF REMOVING CARBON MONOXIDE FROM AIR—There was and is, therefore, no question of the importance of protection against this gas both in war and in peace. Yet at the beginning of these investigations the only effective means known for this purpose was the completely enclosed oxygen helmet—so cumbersome and heavy (40–60 lbs.) that it is burdensome to use even in rescue work—and quite out of the question for men in action. Moreover, it is far too expensive for any wide application.

The reasons why the removal of carbon monoxide from air has been found so difficult lie in the physical and chemical properties of this gas. It has so low a boiling point and critical temperature that one cannot expect adequate adsorption at ordinary temperatures even by an active adsorbent. Thus charcoal under these conditions adsorbs very little of it, little more, indeed, than it does of nitrogen.[2] The known insolubility of carbon monoxide in all solvents similarly precludes its removal by physical absorption.

Chemically, carbon monoxide is decidedly inert at room temperature. Caustic alkalies convert it into formate only when fused or when the solution is strongly heated. Heated sodium amide converts it into cyanide.[3] Solutions of ammoniacal cuprous salts absorb a limited amount of this gas with formation of an addition compound. It is oxidized by many oxidizing agents; but, so far as was known in 1917 when this investigation was started, the reaction is rapid at room temperature only with very powerful and reactive oxidizing agents,[4] such as palladium chloride, gold chloride, platinum chloride, osmic acid and permanganic acid in solution. Certain solids, as silver oxide,[4] yellow mercuric oxide,[4] and cobaltic oxide[1] were also known to react with the pure gas at this temperature, but the reaction was presumably slow at low concentrations of the carbon monoxide. Catalysts for the reaction with gaseous oxygen were known, such as palladium or platinum, but nothing approaching a quantitative removal of carbon monoxide at room temperature had been realized.

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[1] Published by permission of the Director of the Bureau of Mines, and the Director of the Chemical Warfare Service.

[2] The Experiment Station was established by the Bureau of Mines in 1917, and on July 1, 1918, was constituted the Research Division of Chemical Warfare Service. The first investigations (1917) were initiated under the direction of J. F. Norris. As more emphasis was placed upon the problem because of the requirements of the Navy a special Carbon Monoxide Unit was established in December 1917, in the Defense Chemical Research Section, A. B. Lamb, Chief. The work of the coöperating laboratories was also coördinated in this Section. In May 1918 W. C. Bray assumed charge of the Carbon Monoxide Unit in Washington, and was succeeded by R. G. VanName in September 1918.

[1] See Mine Rescue Work, Capt. H. D. Trounce, Engineer Reserve Corps, U. S. A., Professional Memoirs, Corps of Engineers, U. S. A., 10 (1918), 549.

[2] Freundlich, "Kapillarchemie," 1909.

[3] Beilstein and Geuther, *Ann.*, 108 (1858), 88; Gmelin-Kraut, II, 1, 299 (1906).

[4] Abegg, "Handbuch," III, 2, 142–3 (1909); Fay, *et al.*, *Polytech. Eng.*, 10 (1910), 72.

REQUIREMENTS FOR A GOOD ABSORBENT—Nor is mere removal of carbon monoxide by any means the sole requirement of a satisfactory carbon monoxide absorbent. As was pointed out in a recent article entitled "Gas Mask Absorbents,"[2] there are a number of such requirements.

In the first place, the absorbent must have a high activity, that is, because of the considerable velocity and volume of the inhaled air stream in any feasible, portable breathing apparatus, the absorbent must be able to reduce concentrations of carbon monoxide in the inhaled air of, say, 0.2 per cent to 4 per cent down to 0.01 per cent in about one-tenth of a second, and, what proved to be still more difficult, it must be able to do this even at temperatures as low as 0°.

Second, the absorbent must have a considerable absorptive *capacity*. For, on the one hand, the mask must have a "life" of at least an hour or two, that is, it should afford satisfactory protection under ordinary conditions for that length of time. This can, of course, be secured by using large amounts of absorbent. But on the other hand, the size of a portable equipment for men in action is decidedly limited.

Again, the absorbent must offer a low breathing resistance, that is, the wearers of the mask, particularly troops in action, must be able to breathe freely and deeply. This means that only a coarsely porous material or one made up of large granules can be employed, and the consequent limited area of the absorbent means an additional tax upon the activity of the material. The use of a liquid absorbent can be considered only as last resort.

Finally, the absorbent must have a considerable physical and chemical stability. That is, the porous material, presumably granular in nature, must be hard and firm enough to withstand the rough handling and jolts to which it will be subjected in actual field use; it must not crush or be subject to abrasion with the consequent formation of fines. Chemically, the absorbent must be sufficiently permanent to withstand long storage at varying temperatures up to 50° without deterioration. During use it should be unaffected by the normal constituents of the air and should not disintegrate or become deliquescent. If the absorbent should be affected by moisture, provision must be made for drying the entering gases and for keeping the canister tightly closed when not in use.

The problem was, therefore, not merely to find a carbon monoxide absorbent which would react at 0°, but one which would react very rapidly at that temperature, have a considerable capacity, be hard and firm enough to retain a porous structure with rough handling and be chemically stable. Below are given brief accounts of the chief lines of attack, stated approximately in chronological order, which were followed.

ABSORBENTS INVESTIGATED

OZONE—While almost out of the question for use in a portable mask, there was a possibility that ozone electrically generated might be made to react rapidly enough with carbon monoxide to serve as a means of destroying this gas in confined spaces, such as in submarines or in boiler rooms where a permanent ozone generator could be installed. Better still, it was hoped that passage of the carbon monoxide-air mixture through the ozonizer might, by the alternate consumption and re-formation of ozone, result in the oxidation of more carbon monoxide than would correspond to the rates of ozone production of the ozonizer. This possibility was investigated in the fall of 1917 by R. E. Wilson and A. B. Ray at the American University Experiment Station, and later by F. O. Anderegg at the University of Illinois and at Purdue University.

Wilson and Ray found that in a 5 per cent carbon monoxide-air mixture, passed at a rate of 500 cc. in 15 min. through an ozonizer capable of generating 3.5 per cent of ozone in air under the same conditions, a 50 per cent conversion to carbon dioxide occurred at room temperature, while at one-fifth the rate an 85 per cent conversion occurred. When oxygen was used in place of air no oxidation of the carbon monoxide could be detected.[1]

By passing the carbon monoxide-air-ozone mixture after leaving the ozonizer through various catalysts, of which silver, silver oxide, and lead were apparently the best, a more complete oxidation of the carbon monoxide was obtained, so that a 4 per cent carbon monoxide mixture was 80 per cent oxidized in 20 min. and a 0.4 per cent mixture in 10 min.

F. O. Anderegg confirmed the results of Wilson and Ray, but observed that the silver after some time appeared to lose its effectiveness. He also tried introducing silvered asbestos directly into the discharge tube, in the hope of securing a more rapid decomposition and re-formation of ozone, with possibly a more complete oxidation of the carbon monoxide. The results were somewhat irregular but in general this procedure appeared to be disadvantageous, as the ozone concentration was reduced almost to nothing without any apparent effect on the oxidation of the carbon monoxide. No better results were obtained by using a very large (20 liter) corona discharge tube in place of the usual ozonizer tube, and applying an alternating potential of 60,000 volts. In all of these experiments many inexplicable variations occurred, so that a more careful investigation is desirable.

The data obtained by these investigators all indicate that the reaction occurs at best only in stoichiometric proportions, that is, a molecule of ozone is consumed for every molecule of carbon monoxide oxidized. So long as such is the case, this method of eliminating carbon monoxide appears hardly feasible on account of the large and expensive electrical installation required to produce the ozone. Thus, on this basis, to purify 100,000 cu. ft. per hr. of air containing one-tenth of one per cent carbon monoxide would require 200 kilowatts per hour of electric energy, with the most efficient ozonizer.

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[1] Wright and Luff, *J. Chem Soc*, **33** (1878), 1, 504.

[2] Lamb, Wilson and Chaney, THIS JOURNAL, **11** (1919), 420

[1] This confirms the results of Remsen and his students, and of Jones and of Waters. Remsen and Southworth, *Am J. Sci.*, **2** (1876), 136; *Ber.*, **8** (1875), 1414; Remsen, *Am. Chem. J*, **4** (1882), 50; Remsen and Keiser, *Ibid.*, **4** (1888), 454; Leeds, *Ibid.* **5** (1883), 250; W. A Jones, *Ibid.*, **30** (1903), 40; Waters, *Ibid*, **30** (1903), 50. It is not clear, however, whether Jones and Waters used oxygen or air in their experiments

PALLADIUM AS A CATALYST—One of the first methods to give positive results at room temperature was the use of palladium as a catalyst for the combustion of carbon monoxide with the oxygen of the air. This method was studied by a group of men at the University of Chicago, working under the direction of Professor J. Stieglitz. While it was recognized that the limited supply and high cost of palladium were serious handicaps, it was hoped that a method might be developed for using this substance in minute quantities. A large number of experiments were made with finely divided palladium, prepared by reduction under different conditions, and subjected subsequently to different drying and heat treatments. Palladium oxide and mixtures of the oxide with the metal (palladium black) were also tested. Small glass tubes, usually about 3 mm. in diameter, were packed with alternate layers of glass wool and catalyst, 0.2 to 0.7 g. palladium being used in each experiment. Air containing a known amount of carbon monoxide, 0.5 to 3 per cent, dried over soda lime and calcium chloride, was passed through the catalyst rapidly, usually 500 cc. in from 1 to 5 min. Many samples were prepared which initially removed carbon monoxide completely, but the catalysts always "died" more or less rapidly with continued use; others showed a very slight activity. When the catalyst was active a marked heating effect was always observed and it is probable that sintering of the catalytic material was one of the reasons for deterioration. The palladium was also found to be sensitive to impurities, and accordingly the results were not completely reproducible.

In August 1917 similar experiments with asbestos or clay impregnated with palladium were performed at the Bureau of Mines, Pittsburgh, by T. D. Stewart, who came from Chicago for this purpose. The results were not encouraging; the impregnated materials were less active than the palladium alone, and always deteriorated with use.

The activation of certain metal oxides with small amounts of palladium was also considered at several laboratories. Some promising results were obtained with freshly prepared materials, but on account of the known sensitiveness of palladium to impurities, and its cost, the work was not continued. As an example may be cited some experiments at the University of California in January 1918, with a porous copper oxide (apparent density 1.38), which will be referred to later. While alone the copper oxide removed initially only 50 to 20 per cent carbon monoxide from a one per cent mixture with air, in two experiments with material containing 0.25 and 0.4 per cent palladium 95 to 100 per cent were removed initially at room temperature and 80 to 85 per cent after 2 or 3 hrs.' use. A 5-cm. layer of absorbent was employed and the gas was passed through it at the rate of about 2 liters per min. per sq. cm. cross section. A simple calculation shows that the action of the activated material was at least partly catalytic.

The copper oxide granules were impregnated with a dilute solution of palladium nitrate which had been prepared by evaporating a solution in concentrated nitric acid to a small volume and diluting with cold water. The impregnated granules were heated in air at 450° to 500° in an electric oven for a short time before use. In another experiment in which the palladium nitrate solution after dilution was boiled, a flocculent brown precipitate was formed, and the resulting granules showed no activity. It is not known whether this negative result was due to a poisoning of the palladium or to the observed change in the palladium nitrate solution on boiling.

MERCURIC OXIDE AND CHROMIC ACID ANHYDRIDE—In 1917, at Johns Hopkins University, under the direction of J. C. W. Frazer, a large number of oxidizing agents were examined. Yellow mercuric oxide,[1] prepared in the dark, and chromic acid anhydride were found to react slowly at room temperature with carbon monoxide. The discovery was made that a mixture of these was more reactive than either substance alone, and absorbents were prepared which oxidized 70 to 80 per cent of a one per cent carbon monoxide-air mixture for a short time. Further experimentation failed to improve the mixtures materially and work on this absorbent was discontinued. One of the best mixtures was prepared by mixing 100 g. infusorial earth, impregnated with a solution of 100 g. chromic acid anhydride in 300 cc. water, with 5 g. of finely ground mercuric oxide; the mixture was evaporated to a pasty mass on a water bath, mixed with pumice or porcelain granules, and finally dried on a water bath.

SILVER OXIDE—The recognized activity of silver oxide toward carbon monoxide led to its study by several investigators. Stieglitz, early in 1918, found that carbon monoxide in air was rapidly oxidized at room temperature by silver oxide and sodium peroxide arranged in alternate layers in a glass tube. The silver oxide was precipitated from a dilute solution of silver nitrate by the addition of a barium hydroxide solution in about one per cent excess, with constant shaking during precipitation. The precipitate was washed two or three times by decantation, filtered, pressed together on the filter, dried at 85° to 120°, and finally heated to 200°. It was shielded from carbon dioxide throughout this treatment. The final product was in the form of rather soft lumps, which were easily crushed to the required size. The silver oxide and sodium peroxide in equal parts were placed in alternate layers, separated by glass wool, in glass tubes either 1 cm. or 3.2 cm. in diameter, to depths not exceeding 10 cm. At room temperature carbon monoxide at concentrations between 0.5 and 4.5 per cent was about 98 per cent absorbed when 500 cc. samples of gas were passed in 0.5 to 2 min. Similar results were obtained with intermittent flow. At 0° the reaction started fairly rapidly but not instantaneously.

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[1] Colson, *Compt. rend.*, **132** (1901), 467.

At room temperature neither of the two ingredients alone rapidly oxidizes carbon monoxide at a low concentration in air. Silver oxide is much more reactive than sodium peroxide; when it is heated to 40° or 50° the reaction starts rapidly and continues without further application of heat on account of the heat generated in the reaction. The interesting question as to why the mixture operates so much better than the silver oxide alone cannot be answered with certainty, but it is probable that the function of the sodium peroxide is to remove the carbon dioxide formed, and thus prevent the formation of silver carbonate on the surface of the silver oxide. The net reaction is the formation of sodium carbonate and silver. Also when the gas is not completely dry the heat of the reaction between water and sodium peroxide serves to raise the temperature of the absorbent, and thus increase its activity. It was in fact observed that the presence of moisture in small amounts in the gas had a beneficial effect.

Similarly, Frazer, late in 1917, studied a mixture of silver oxide and calcium hydroxide. Silver oxide precipitated and washed cold was mixed with calcium hydroxide as a thick paste, the mixture was dried on a steam bath and then heated to 110° in a current of oxygen for about 2 hrs. For a mixture containing silver oxide and calcium hydroxide in the proportion of 1 to 5 by weight, a laboratory test with one per cent carbon monoxide showed 90 per cent removal of carbon monoxide at the end of 5 min.; and a canister test showed 80 per cent efficiency at the end of 10 min., and 60 per cent efficiency at the end of 22 min. This material is evidently much less satisfactory than the silver oxide-sodium peroxide mixture, though it is not improbable that the function of the calcium hydroxide (or oxide) is similar to that of the sodium.

Meanwhile, as will be shown later, the possibility of using relatively small amounts of silver oxide to activate certain metallic oxides or mixtures of oxides had been demonstrated. On account of the lower cost of these materials, absorbents rich in silver, such as the above, could not be considered. It may also be added that, since firm granules of silver oxide and sodium peroxide are not easily made, the resistance of the mixture in a canister to the flow of gas would have been unduly high.

IODINE PENTOXIDE—Iodine pentoxide is specifically active in oxidizing carbon monoxide, and advantage has long been taken of this fact in the analysis of carbon monoxide-air mixtures. C. R. Hoover and A. B. Lamb, in September 1917, tested the efficacy of various metals, metallic oxides, and acidic oxides and acids as catalysts in this reaction. It was found that strongly oxidizing or dehydrating acidic oxides, such as sulfur trioxide and phosphorus pentoxide, and concentrated nitric, sulfuric, and phosphoric acids and mixtures with their anhydrides, had marked accelerating effects independent of any moisture in the gas, so that the oxidation would occur rapidly at room temperature, and in the most favorable instances even at 0° C.

Fuming sulfuric acid was found to give the most active mixture with iodine pentoxide, and pumice was found to be the most suitable base on which to support it. Careful investigations were carried on by C. R. Hoover at Middletown, and under the direction of A. W. Kenney, R. G. VanName, and particularly W. C. Bray, at the Washington laboratory, on the optimum proportions of sulfur trioxide, water, iodine pentoxide, and pumice, to afford the maximum life, the most complete of oxidation, the quickest start ("pick up") of the reaction, and the least concentration of sulfur trioxide in the effluent air.[1]

Using a layer 10 cm. deep of a favorable mixture and passing a one per cent carbon monoxide-air mixture at the rate of 500 cc. per min. per sq. cm. cross-section (corresponding to rapid breathing through a gas mask of the usual dimensions), a 100 per cent to 90 per cent removal of carbon monoxide could be secured for 2 hrs. at room temperature, and almost as long at 0° C. This corresponds to a 75 to 80 per cent utilization of the iodine pentoxide.

The action is not instantaneous, and a brief induction period always occurs. At room temperature with one per cent carbon monoxide this is very brief, so that the "pick up" requires but a fraction of a minute, but at 0° it may require several minutes, and at lower concentrations still longer before absorption becomes substantially complete. This would allow an initial leakage of carbon monoxide which might well be dangerous.

However, it was shown that the active agent in the oxidation of the carbon monoxide is an intermediate compound, and the time required for the formation of an adequate amount of it is responsible for the existence of the period of induction. It was further shown that this same substance, or one similar to it, can be produced by the addition of a little iodine to the original mixture. By a preliminary treatment of this kind the "pick up" is materially improved, so that with a one per cent gas at 0° the induction period lasts less than one minute. No serious initial leakage of carbon monoxide, therefore, can occur with this active material.[2]

The sulfur trioxide given off is, of course, very irritating to the lungs, but by the use of a layer of active charcoal beyond the carbon monoxide absorbent this disadvantage was very completely eliminated. However, sulfur dioxide is slowly formed as a result of this adsorption, and after prolonged standing or long-continued use of the canister at a high rate gives serious trouble. This is partially remedied by the use of a soda lime-charcoal mixture, and could doubtless be more completely eradicated by the substitution of a chemically inert absorbent, such as silica-gel, for the charcoal.

Considerable heat is given off in this reaction and a cooling attachment was required. The most satisfactory devices were a metal box filled with fused sodium thiosulfate pentahydrâte which in melting absorbed a very considerable amount of heat, or a long, flexible, metallic tube between the canister and the mouth, which cooled the effluent gases very effectively, or finally, a moistened sponge placed in the breathing tube between the absorbent and the mouth. This last not only cooled the air, but also humidified it and so obviated the somewhat irritating effect of the prolonged breathing of very dry air. This absorbent had the further disadvantage that it became spent by use, even in the absence of carbon monoxide, since it absorbed enough moisture from air of average humidity in several hours to destroy its activity.

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[1] Later it was learned that the French had discovered and utilized the activating effect of sulfuric acid on the reaction between carbon monoxide and iodine pentoxide, though no mention of the use of fuming acid was made

[2] "Hoolamite," U. S Patent 1,321,061.

These difficulties of sulfur trioxide formation, heat evolution, and moisture absorption were so troublesome that this absorbent was finally supplanted by the more satisfactory metallic oxide absorbent to be described later.

Incidentally a simple and inexpensive method for the production of very pure iodic anhydride was perfected; also it was shown that the green color resulting from the action of carbon monoxide on the iodine pentoxide-fuming sulfuric acid-pumice mixture (Hoolamite) could be used as a very sensitive detector for the presence of carbon monoxide in air.[1]

SILVER PERMANGANATE—An investigation of the oxidation of carbon monoxide by silver permanganate by Ernest Bateman, of the Forest Products Laboratory, begun in November 1917, led to some interesting results. While moist one per cent carbon monoxide was not oxidized rapidly by silver permanganate alone, the reaction was very fast when solid calcium chloride was mixed with the permanganate, and the reaction usually culminated in an explosion before the permanganate was completely reduced. By mixing in a third ingredient, calcium oxide, and by avoiding the use of a large proportion of calcium chloride, a relatively safe absorbent was made, which had a long "life"—2 to 4 hrs. in the standard tests with one per cent carbon monoxide. The oxidation of the carbon monoxide was practically complete. The best proportions were, by weight, 85 parts $AgMnO_4$, 15 parts CaO, and 15 to 20 parts $CaCl_2$. The dry materials were ground together in a mortar and pressed together into a cake under high pressure; the cake was then broken up and meshed to granules of the required size. The presence of moisture in the entering gas was essential for satisfactory operation. The first tests at 0° gave unsatisfactory results, and on this account the work was discontinued for some months. Later it was found that the poor results at 0° were due to the low moisture content of the cold gas. By providing for humidification of the entering gas, *e. g.*, with an agar jelly or suitable hydrated salt, the absorbent was made to operate efficiently at 0°.

At the time that this very promising result was obtained in Madison, July 1918, intensive work had already been started in Washington on the absorbent finally selected, Hopcalite, which functioned as a catalyst for the oxidation of carbon monoxide by the oxygen of the air. On account of the pressure of this work it was not possible to continue in Washington the study of this other absorbent. We have, therefore, no data on the preparation of the material on a large scale, on canister tests, or on the durability or safety of the material when stored. The considerable expense of this absorbent and the fact that it is not catalytic and so is consumed in use are serious drawbacks.

METALLIC OXIDE MIXTURES

COPPER OXIDE AND SILVER OXIDE—In the fall of 1917, G. N. Lewis, T. D. Stewart, C. C. Scalione, and D. R. Merrill, at the University of California, found that a specially prepared, precipitated copper oxide activated with one per cent silver oxide, was an efficient catalyst for the oxidation of arsine by the oxygen of the air. Following this clue, the two last-named investigators, with W. C. Bray, found that the mixtures which were most effective for arsine were also most reactive toward carbon monoxide-air mixtures. However, only 50 per cent of the carbon monoxide was removed even at the start, the "life" of the absorbent was short and the action appeared chemical rather than catalytic.

The activity of the material was not increased by increasing the silver content above one per cent. Though these results were, therefore, far from satisfactory, they showed that the physical state of the absorbent was a controlling factor. It was evident that a highly porous and yet hard granule was the goal to be striven for.[1]

COPPER OXIDE AND COBALTIC OXIDE—Other more active oxidizing agents were now studied from this same point of view, and in particular, influenced by the work of Wright and Luff,[2] cobaltic oxide and manganese dioxide were selected; and it was decided to study the influence of the physical nature of the granules by varying the method of preparation, and to investigate the behavior of mixtures of oxides.

The method of preparation was based on that used by Hüttner[3] and consisted in treating cobaltous sulfate solution at room temperature with excess of a mixture of sodium hypochlorite and sodium hydroxide. The mixture was allowed to stand for one-half hour, in which time the excess hypochlorite was catalytically decomposed. The hydrated oxide was thoroughly washed by decantation and filtered, dried at 120°, and meshed in the usual way. The oxygen content of the oxide was uniformly somewhat greater than would correspond with the formula Co_2O_3, indicating the presence of some CoO_2.

The behavior of different samples of cobalt oxide granules toward one per cent carbon monoxide was variable in the extreme. Changes in the method of preparation had a great effect on the physical nature of the granules; the apparent density, for example, varying from 0.7 to 1.4. Better results were obtained in the test with dry one per cent carbon monoxide than with moist gas, but the life of the absorbent was usually short and in only a few instances was as long as one hour. With dry gas the initial efficiency varied from 15 per cent to nearly 100 per cent, but the results were not reproducible.[1]

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[1] Forthcoming paper; also U. S. Patent 1,321,062.

[1] The method of preparation is appended because it illustrates the procedure used in the subsequent work. Copper sulfate solution was added to sodium hydroxide solution at a temperature from 70° to 100°. When excess sodium hydroxide was used this was neutralized by the addition of dilute sulfuric acid to the hot mixture; in later work the same results were accomplished by decreasing the amount of sodium hydroxide originally used. In all cases the precipitates were freed from salts by thorough washings, usually by decantation. The hydrated oxide sludge was impregnated with silver oxide by stirring in the desired amount of silver nitrate solution and adding a sufficient quantity of sodium hydroxide solution. The mixture was washed twice by decantation and collected as a filter cake on a Büchner funnel or in a filter press. The cake was dried slowly in an air oven up to 120°, crushed and meshed, the 10- to 14-mesh material being used in the tests.

[2] *J. Chem. Soc.*, **33** (1881), 1, 504.

[3] *Z. anorg. Chem.*, **27** (1901), 81.

To test whether mixtures were more active than the single components, a mixture of 60 per cent active copper oxide and 40 per cent active cobaltic oxide was prepared from an intimate mixture of the moist hydrated oxides and was tested at Berkeley in March 1918. It operated at fairly high efficiency, had a long "life" (about 2 hrs.), and was apparently partially catalytic, since the decrease in available oxygen during the run was insufficient to account for all the carbon monoxide oxidized.

MANGANESE DIOXIDE AND SILVER OXIDE—A similar development of oxide absorbents had also been carried on at Johns Hopkins University by J. C. W Frazer and his assistants. They had proved that, while neither manganese dioxide nor silver oxide reacted rapidly at room temperature with one per cent carbon monoxide, mixtures of them from the beginning gave encouraging results. At first sodium hydroxide was included as an ingredient in the mixtures and it was found that the reactivity increased with increasing amount of it, at least up to 12 or 15 per cent. The presence of small amounts of fused granular calcium chloride in layers in the absorption tube increased the life of the absorbent. At room temperature with dry one per cent carbon monoxide, under standard conditions of testing, the removal of carbon monoxide was practically complete with the best mixtures for from 30 to 40 min. and these absorbents, even in the absence of calcium chloride, continued to operate for 10 to 15 min. longer before the efficiency fell to 90 per cent, that is, until the amount of unabsorbed carbon monoxide reached 10 per cent. Tube tests indicated that the presence of moisture in the gas increased the life of an absorbent. At 0° the materials operated at high efficiency, but for a shorter time. The action in all cases was apparently the oxidation of carbon monoxide by the silver oxide and manganese dioxide. All the active mixtures contained a greater weight of silver oxide than of manganese dioxide and satisfactory results were obtained when the proportion of silver oxide to manganese dioxide was 1.5–2.5 to 1.

These investigators found that the efficiencies varied greatly with the physical character of the manganese dioxide. The above reproducible results were obtained with material prepared by the action of methyl alcohol on a solution of potassium permanganate, heated to 75°.[2]

Slightly better results were obtained with a three component mixture containing cobaltic oxide, silver oxide, and manganese dioxide in the proportions of 1 : 1 : 0.5 to 1, respectively, the "life" being longer than one hour against dry one per cent gas. Sodium hydroxide was found to be undesirable in such mixtures and was omitted. When a smaller proportion of silver oxide was used the materials were much less active.

HOPCALITE—By May 1918, the group at the University of California had all been transferred to Washington, D. C., and from that time on there was active collaboration between the Washington and the Baltimore laboratories, that is, between the two groups engaged on the study of mixtures of metallic oxides.

At the Johns Hopkins laboratory it was soon found that much more active varieties of manganese dioxide could be prepared and that the omission of sodium hydroxide from the mixtures of silver oxide and manganese dioxide then increased the life. The first really active manganese dioxide was prepared by reducing with methyl alcohol a cold solution of ammonium permanganate instead of the potassium salt. Much more finely divided manganese dioxide was obtained, and the life of a mixture of equal parts of this material and silver oxide was over 3 hrs. Finally, with manganese dioxide prepared by the Fremy method[1] where potassium permanganate was treated with a cooled mixture of concentrated sulfuric acid with 0.3 of its weight of water,[2] the discovery was made that with dry gas the action of a mixture of equal parts of manganese dioxide and silver oxide became *catalytic*, that is, the carbon monoxide was oxidized continuously *by the oxygen of the air*.

Simultaneously, in the Washington laboratory, Bray, Scalione, and Merrill discovered an equally active catalyst consisting of a three component mixture of cobaltic oxide, manganese dioxide, and silver oxide, in the proportion of 20 : 34 : 46, which was prepared by the interaction of silver permanganate with moist hydrated cobaltic oxide.

The catalytic behavior of these mixtures against dry one per cent carbon monoxide was at once verified in both laboratories. The behavior of fresh samples of the manganese dioxide-silver oxide mixture was found to be identical with that of the first sample. While this catalyst had an apparently indefinite life with dry gas, moist gas "killed" it fairly rapidly and the amount of available oxygen in the material was found to decrease at the same time. However, it revived very quickly when again treated with dry gas. This behavior towards moisture was found to be characteristic of all catalysts subsequently prepared, and was used as a criterion for catalytic behavior.

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[1] It was later, in August, found that these inconsistencies were chiefly due to differences in the method of drying.

[2] The suspended manganese dioxide was collected on a filter and washed 3 times with distilled water; the paste was dried until it contained about 50 per cent water, which was accurately determined and allowed for in making up the mixtures. The manganese dioxide paste was mixed with water and stirred until a uniform suspension was obtained. This was added with stirring to a silver nitrate solution containing sufficient silver nitrate to give the desired amount of silver oxide. The sodium hydroxide solution was added with vigorous stirring until a distinct alkaline reaction was observed The brownish yellow mixture was stirred until it became dark brown, or almost black in color. The material was washed three times by decantation and collected as a filter cake on a Büchner funnel. To this cake the required amount of sodium hydroxide in solution was added and mixed in by stirring. The material was dried on a water bath, broken up, and finally dried for about 3 hrs. at 140° in a current of dry oxygen. It was ground and meshed, 10- to 20-mesh granules being used in the tests.

[1] *Compt rend.*, **82** (1876), 1231.

[2] The mixture was allowed to stand for several days during which time the permanganic acid slowly decomposed with evolution of oxygen. The mixture was then poured into a large volume of water and the resulting finely divided manganese dioxide washed, first by decantation and then on a filter, until the filtrate showed no test for sulfate.

A large variety of mixtures of the above-mentioned oxides were then investigated. In their preparation, the hydrated oxides were usually prepared separately, washed thoroughly, and intimately mixed. When impregnation with small amounts of silver oxide was desired, the necessary amount of silver nitrate solution was stirred in, and enough sodium hydroxide added to precipitate the silver oxide. The final material was always thoroughly washed, collected in a funnel or in a filter press, dried slowly up to 120°–130°, meshed, and finally dried at 200°. In all subsequent treatment exposure to moist air was, of course, avoided.

The method of drying was important and it was found that the amount of water of hydration left in the granules was a determining factor in the preparation of active catalysts. In general much better results were obtained when the granules were heated for a short time at 200°, after the preliminary slow drying up to 120° or 130°. This was especially important for mixtures containing the highly hydrated cobaltic oxide, and a number of such mixtures behaved as catalysts only after this heat treatment. In fact cobaltic oxide itself when treated in this way acted catalytically, and furnished the only example to date of a catalyst at room temperature which consists of a single oxide. Prolonged heat treatment at a high temperature, on the other hand, spoils these catalysts, presumably on account of the destruction of the porous nature of the granules. Materials containing a large amount of silver oxide are apparently more easily injured by heating.

As has already been indicated, it was necessary to determine carefully the exact conditions for the preparation of each oxide in the most suitable form. It may be said, in general, that the physical state of the final granules and the behavior of the catalyst, depend upon the size and composition of the particles of which the original precipitates are composed. If the particles are extremely fine, and are not made to clump together or combine before filtration, hard and relatively non-porous granules result, which are less active as catalysts than are more porous granules. On the other hand, if the particles are too coarse, soft though usually active granules are obtained, which are not robust enough for use in canisters. The latter condition can be remedied to a considerable extent by subjecting the filter cake to high pressure before drying it.

The granules are very porous, and the action of the catalysts at low temperatures is believed to be dependent on the large surface exposed to the carbon monoxide and oxygen. 100 cc. of 14–16 mesh granules of one sample of this material were found by Dr. G. A. Hulett, of Princeton, to contain only 8.8 cc. of solid material, while the volume of the large spaces between the granules was about 47 cc. This left a capillary volume of about 44 cc. The high porosity, also, must be responsible for the poisoning effect of water vapor, which was observed with all catalytic mixtures at room temperatures. The decreasing effect of the water vapor at high temperature is in agreement with this view.

The best catalysts contained active manganese dioxide as the chief constituent. While this substance prepared by the Fremy method seemed better than that from the ammonium permanganate-methyl alcohol method, the latter material was found to be satisfactory. A third method of preparation was developed in the Washington laboratory, which was similar to that covered by a German patent[1] and depended on the reaction between potassium permanganate and anhydrous manganese sulfate in the presence of fairly concentrated sulfuric acid. This method is the one that was used in the preparation of active manganese dioxide on a large scale. It may be mentioned that manganese dioxide did not prove satisfactory when prepared by the oxidation of the manganous salt in neutral or alkaline solution; that is, mixtures made from it usually were not catalytic. Active copper oxide and cobaltic oxides were prepared on a large scale by the methods previously mentioned.

Many mixtures of widely different composition show catalytic behavior and the possible range of compositions seems to increase with the number of components. Thus, for a comparable series of mixtures in each of which manganese dioxide is the chief constituent, the minimum silver oxide content necessary to ensure catalytic action decreases progressively as the number of components increases from 2 to 3 to 4. The limit is about 38 per cent Ag_2O in the two component mixtures, about 15 per cent in the three component mixtures containing copper oxide, and 5 per cent or less when cobalt oxide also is present.

A four component mixture containing 50 per cent MnO_2, 30 per cent CuO, 15 per cent Co_2O_3 and 5 per cent Ag_2O was chosen in August as a standard catalyst to be tested on a larger scale. This particular mixture was named Hopcalite I, Hopcalite being used to designate any catalyst of this type. A small scale manufacturing plant was built and operated at the American University Experiment Station; tube tests and canister tests proved that the resulting material behaved as well as that which had been prepared on a small scale in the laboratory. This material acted as a catalyst at 0° with as low a concentration of carbon monoxide as 0.2 per cent when the tests were made with dry gas.

While this work of development was in progress, the search for a cheaper catalyst was continued in both laboratories. The most promising material discovered was a two component mixture of MnO_2 (60 per cent) and CuO (40 per cent), developed in the Baltimore laboratory, which was prepared from active manganese dioxide and copper carbonate. The latter was transformed almost completely into the oxide in the drying process. However, this material was still in the laboratory stage of development in September, when it was necessary to decide what mixture would be used in large scale production; and the four component mixture was chosen for this purpose.

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[1] Bad An. Sod. Fab. D. R. P. 163,813 (1905); *Z. Elektrochem.*, 11 (1905), 853.

THE MANUFACTURE OF HOPCALITE I

The particular mixture of oxide selected for large scale[1] manufacture, on the basis of the extensive laboratory and small scale manufacturing tests, had the components MnO_2 50 per cent, CuO 30 per cent, Co_2O_3 15 per cent, and Ag_2O 5 per cent, as mentioned above. The process of manufacture was merely an extension of what had proved the best laboratory technique, namely, the separate precipitation and washing of the manganese dioxide, copper oxide, and cobaltic oxide, and the subsequent precipitation of the silver oxide in the mixed sludge. After further washing the sludge was run through a filter press, kneaded in a machine, and the cake dried and ground to size. The fines were ball-milled wet and re-pressed.

While it was not difficult to obtain a product which was catalytically active, it required a rigorous control of all the conditions and operations to assure a product at once active, hard, dense, and as resistant as possible to the deleterious action of water vapor. The temperatures, concentrations, rates of additions, stirring, etc., during the precipitations particularly that of the manganese dioxide, had to be carefully studied and controlled. The precipitates had to be washed very carefully by decantation down to the point at which they began to be colloidal; the kneading of the pulp had to be sufficient but not prolonged; the drying had to be carried out according to a carefully regulated schedule; and, finally, since the material at best is comparatively soft, much study and attention had to be given to the grinding and sieving to prevent the formation of an excessive amount of fines.

These difficulties were all eventually overcome, and a plant was constructed and operated in coöperation with the Rare Metal Products Company at their works at Belleville, N. J., under the immediate supervision of D. R. Merrill and A. T. Larson. This plant had a daily capacity of 500 lbs. of finished product.

The product was required to meet the following rigorous tests: A screen analysis must show not more than 15 per cent above 8 mesh; at least 52 per cent 8–12 mesh; not more than 6 per cent 14–16 mesh and not more than 2 per cent less than 16 mesh. The apparent density of an 8–14 mesh sample must be at least 0.55. The hardness had to meet a definite test on the Rotap machine, corresponding to rough handling in the field. Rapidity of starting, that is, a quick "pick up," was assured by requiring that a layer 5 cm. deep should initially remove at 20° not less than 90 per cent of the carbon monoxide from a dry 0.25 per cent carbon monoxide-air mixture flowing at a rate of 500 cc. per sq. cm. cross-section per min. True catalytic behavior was assured by requiring that this sample should continue at least 90 per cent efficient for a further period of 3 hrs. against a dry one per cent gas. Finally, the best possible behavior against moist gas was assured by requiring that it should not drop below 85 per cent efficiency when tested, at the same temperatures and rates of flow as with the dry gas, against a one per cent gas containing water vapor at a pressure of 14 mm. mercury.

These tests against carbon monoxide-air mixtures required rapid and frequent analyses of the affluent and effluent air mixtures. By the very slow iodine pentoxide method, which was the only known method sufficiently accurate for the requirements, these analyses would have been very difficult to execute. Fortunately, a rapid calorimetric method had already been developed at the Washington laboratory by Larson and Lamb[1] which permitted a continuous and nearly instantaneous analysis of the affluent and effluent gas streams. This greatly facilitated and accelerated the development of the large scale manufacture.

USE OF HOPCALITE IN CANISTERS—Hopcalite has several characteristics which necessitate certain and permit other modifications in the usual gas mask canister. In the first place, since its action is normally a catalytic one, there is but slight advantage in any considerable depth of absorbent. A depth sufficient to insure close contact of all the air with the catalyst, that is, to avoid any so-called channeling is all that is required. One and a half inches were found ample for the purpose and as a result only about 300 g. of absorbent were required per canister.

In the second place, the normal catalytic activity of Hopcalite requires a dry gas mixture. A drier had therefore to be provided at the inlet side of each canister, and since the life of the Hopcalite and, therefore, of the canister, depends upon that of the drier, as much as possible of it was used, enough indeed to give a layer 3 in. deep. After extensive experiments with a variety of drying materials, a specially prepared, dry, granular calcium chloride was chosen. With a drier of this material and with the affluent air flowing at the rate of 32 liters per min. and containing water vapor at a pressure of 14 mm. mercury, the vapor pressure of water in the effluent air did not rise to 4 mm. mercury until after a lapse of 3 hrs.

Finally, there is an evolution of sufficient heat in the catalytic oxidation of a one per cent carbon monoxide-air mixture to raise its temperature adiabatically about 100°. There is also a considerable heating effect when moisture is absorbed by the drier. However, because of the considerable heat capacity of the canister and its contents, and because of the rapid dissipation of heat by radiation and conduction, the temperature of the effluent air does not rise higher than 50° during the first 15 min. run against a one per cent mixture, and never exceeds 90° even after several hours. An exposure of more than 15 min. to so concentrated a gas as this is unlikely, so that for most purposes the temperature rise would be of no consequence; but to insure a still greater margin of safety additional cooling was provided. This consisted of a small hermetically sealed metal box containing 130 g. of sodium thiosulfate pentahydrate placed between the calcium chloride and the Hopcalite layers.

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[1] **Fifteen tons of the material were required for the Navy carbon monoxide canister.**

[1] ***J. Am. Chem. Soc.*, 51 (1919), 1968.**

The thiosulfate melting at 48° absorbed about 110,000 cal. of heat, and so reduced considerably the rate of temperature increase in the effluent air.

At first, one in every 100 and later one in every 200 of the manufactured canisters was run against 0.5 or one per cent carbon monoxide-air mixtures containing water vapor at a pressure of 14 mm. mercury and at the rate of 32 liters per min. No canister or the lot it represented was accepted which showed a leakage of 0.1 per cent carbon monoxide within 2 hrs.; actually the average life was over 3 hrs. It was found that the higher the temperature the longer the life, which agrees with the fact previously mentioned that Hopcalite is less sensitive to water vapor at higher temperatures. It was further found that the net life of the canister was the same irrespective of whether its use was continuous or intermittent, that is, no deterioration occurred when a partially spent canister was allowed to stand.

ESTIMATED SERVICE TIME IN HOURS FOR HC CARBON MONOXIDE NAVY CANISTER

FOR MEN	Temp. ° F.	Relative Humidity			
		25%	50%	75%	100%
At Rest	32	60	40	24[1]	18
	50	40	24	16	12
	75	24	12	8	6
	100	12	6	4	3
In Action	32	15	10	6	4.5
	50	10	6	4	3
	75	6	3	2[2]	1.5
	100	3	1.5	1[3]	0.75

[1] Ordinary winter conditions on deck.
[2] Summer conditions on deck.
[3] Engine (boiler) room conditions.

In agreement with the fact that the Hopcalite absorbent functions indefinitely against any concentration of carbon monoxide, provided the effluent air is adequately dried, and hence that the life of the canister is limited solely by the life of the drier, it was found that the net gain in weight of the canister was a sure criterion of its condition. At the time of a breakdown, that is, when the leakage reached 0.1 per cent, as tested by the above-mentioned routine method, the average gain in weight of all canisters was 54 g.; none gained more than 71 g. and none less than 42 g. It was recommended, therefore, that any canister which had gained more than 35 g. above its original weight stamped on the canister should be withdrawn.

Since it is the absorption of water which limits the activity of these canisters, the lower the actual humidity of the air in which the canister is used the longer its life. The accompanying table was, therefore, prepared of the estimated service times of these canisters in use on shipboard under conditions which men both at rest and in action might reasonably encounter.

THE PREPARATION OF ARSENIC TRICHLORIDE FROM WHITE ARSENIC AND PHOSGENE[1]

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Received November 3, 1919

INTRODUCTION

At Edgewood Arsenal phosgene was manufactured for use as a war gas by the direct union of carbon monoxide and chlorine in the presence of carbon. It was condensed at about —20° C. under atmospheric pressure, but considerable phosgene was lost in the "tail gas" from the condensers. Means were sought to recover the phosgene in this tail gas and convert it into a commercially valuable product.

It was suggested that this phosgene might be satisfactorily converted into arsenic trichloride by reaction with arsenic trioxide ("white arsenic"). Tests showed that this reaction proceeded very slowly up to the subliming temperatures of arsenic trioxide, and the results were not satisfactory. Experiments made with catalyzers, however, showed that very satisfactory conversion was obtained in the presence of carbon. This paper gives an account of the work done in this connection.

HISTORICAL

The reaction between phosgene and inorganic oxides and sulfides has been studied in detail by Chauvenet.[1] A great number of oxides and sulfides were used, but arsenic was not among them. The reaction was carried out simply by heating the inorganic compound in a tube to a temperature which varied from 300° to 1400° C. according to the material, and passing the phosgene gas over it. Chlorides, and sometimes oxychlorides, were produced, the general reactions being:

$$MO + COCl_2 \longrightarrow MCl_2 + CO_2$$

$$MS + COCl_2 \longrightarrow MCl_2 + COS$$

No catalyzer was used.

Riban,[2] many years before, found that when chlorine is passed over a mixture of tricalcium phosphate and carbon, or when chlorine and carbon monoxide are passed over tricalcium phosphate alone, heated to incipient redness, a small quantity of calcium chloride and *m*-phosphate is formed, but no further change takes place. When, however, carbon monoxide and chlorine together are passed over a heated mixture of calcium phosphate and carbon (boneblack) at 330° to 340° C., $POCl_3$, $CaCl_2$ and CO_2 are produced in quantity. He thought that the carbon acted as a catalyzer by condensing the gases in its pores, and suggested that this reaction might be applied to phosphates in general and to irreducible oxides, like Al_2O_3, from which $AlCl_3$ could be produced. However, he made no experiments using phosgene instead of the mixture of carbon monoxide and chlorine—nor did he attempt to decompose arsenic compounds.

EXPERIMENTAL

LABORATORY EXPERIMENTS—Experiments were made in the laboratory as follows:

Phosgene (analyzing 99.7 per cent $COCl_2$). from a small tank, was dried with sulfuric acid, measured in a flow meter (calibrated for phosgene), and then mixed with air which had been dried and metered in a similar manner. The resulting mixture was run through a Pyrex glass tube containing the charge, generally a mixture of white arsenic and carbon. The tube was heated in an electric oven, and the temperature measured by a long thermometer which reached to the center of the charge inside the tube. The arsenic trichloride formed was collected in a receiver and the exit gases run to waste through a reflux condenser. The charge was prepared from dry materials, but at the beginning of each experiment dry air was passed through the heated tube in order to drive out any remaining traces of moisture.

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[1] This article has been approved for publication by Major-General William L. Sibert, Director of the Chemical Warfare Service, U. S. A.

[1] *Compt. rend.*, **152** (1911), 87, 1250; Barlot and Chauvenet, *Ibid.*, **157** (1913), 1153.

[2] *Ibid.*, **95** (1882), 1160; **157** (1913), 1432.

The phosgene and carbon dioxide in the ingoing and outgoing gas were determined by analyses made on a measured volume of gas collected over mercury. The $COCl_2$ and CO_2 were absorbed in one per cent aqueous sodium hydroxide and the contraction in volume noted; the volume of the $COCl_2$ was calculated from the chloride content of the solution, as determined by titration (Mohr's method) after neutralization with normal nitric acid; the CO_2 was obtained by difference. Analysis of known mixtures gave satisfactory results.

Table I gives a summary of the results obtained in different experiments, each of which was run for about 5 hrs. Very concordant analyses were obtained in each test. It was found that the reaction did not proceed well at low temperatures, and a temperature of 200° C. was therefore used.

TABLE I—LABORATORY TESTS OF THE REACTION BETWEEN PHOSGENE AND WHITE ARSENIC

Temperature, 200° C.
Tube, 1 7 cm internal diameter
Length of charge, 30 cm.[1]

	Charge (per cent by weight)		Ingoing Gas (cc. per min.)		Outgoing Gas (per cent by volume)	
TEST NO.	As_2O_3	Carbon[2]	$COCl_2$	Air	$COCl_2$	CO_2
21	100	0	5	0	43.1	45.0
15	80	20	5	0	0.5	95.0
19	80	20	5	20	2.8	17.5
20[1]	80	20	5	20	0.2	20.9

[1] For Test 20 the tube was completely filled with the charge for a distance of 40 cm. In the other tests the carbon and white arsenic were ground together. For this test a mixture of As_2O_3 with 1/8 in. pieces of carbon, was used.

[2] A variety of carbon know commercially as "filt-char" was used for most of the tests.

The arsenic trichloride produced was water-white and pure, except that it contained a small quantity of dissolved phosgene.[1] With a proper rate of gas flow, the phosgene in phosgene-air mixtures was almost completely removed.

PLANT EXPERIMENTS—An apparatus very similar to the one used in the laboratory, but built of iron pipe was used for small scale works experiments. The furnace was made from a 5-ft. length of 4-in. pipe and was electrically heated by a resistance ribbon winding, and insulated with magnesia asbestos pipe covering. The caps at the ends of the pipe were drilled and threaded for inlet and outlet, respectively, and each contained a thermometer well. The temperature was controlled by a water rheostat in the electric circuit. A water-cooled condenser with a trap and a receiver was attached to the exit end of the furnace. The apparatus was operated by suction; "tail gas" from the phosgene plant condensers was drawn in succession through a flow meter, through the furnace containing the charge, through the condenser and the trap. Sampling cocks were placed on the inlet and outlet lines.

The entering and exit gas was analyzed from time to time for phosgene and carbon dioxide, as previously described. An average tail gas entering the apparatus contained 35 per cent $COCl_2$. Carbon monoxide, carbon dioxide and traces of chlorine and water vapor were also present. Although no tests were made for hydrochloric acid, it is probable that a small amount was present.

The condensate separated in two layers, arsenic trichloride below and water on top, both being colored red-brown by iron. The iron in the $AsCl_3$ was determined colorimetrically.[1] The water layer was analyzed for arsenic and iron gravimetrically, and for chloride by Volhard's method. The arsenic and iron were calculated as chlorides, the residual chloride as hydrochloric acid, and the rest of the sample assumed to be water.

The results of the experiments with a charge containing by weight 80 per cent As_2O_3 and 20 per cent filt-char are given in Table II:

TABLE II—EXPERIMENTS WITH SMALL SCALE WORKS APPARATUS FOR ARSENIC TRICHLORIDE FROM PHOSGENE TAIL GAS

Charge, 80 per cent As_2O_3 and 20 per cent filt-char

Test Number	3	*4b*	*4c*	*5a*	*5b*
Duration of Experiment (hrs.)	4.25	4.5	2	3	2
Average Temp. (° C.)	200	200	260	260	260
Rate Ingoing Gas (cu. ft. per min.)	0.10	0.05	0.05	0.05	0.10
Average per cent $COCl_2$ in Ingoing Gas	33	39	37	38	38
Average per cent $COCl_2$ in Exit Gas	16	10	1.3	0.7	15
G. $COCl_2$ Used up per hr.	117	110		128	159
Theoretical g. $AsCl_3$ per hr.	143	134		156	194
Actual g. $AsCl_3$ per hr.	106	113		121	146
Per cent Yield	74	85		78	75
G. Water Layer per hr.	25	25		13	19

The weight of the arsenic trichloride was obtained after separation from the water layer with a separatory funnel. An average sample contained 0.05 g. of iron per liter, and a small amount of dissolved phosgene.

A typical analysis of the water layer was:

$AsCl_3$	35.3 per cent
HCl	14.6 per cent
$FeCl_3$	0.8 per cent
H_2O (by difference)	49.3 per cent

The yields obtained were remarkably good, especially since the calculation was based on the average chloride content of the ingoing gas. Quite a little more arsenic trichloride would have been obtained had there been no water layer in the condensate. No arsenic or arsenic trioxide sublimed out of the furnace, although the filt-char was found to be bound together in lumps, when the furnace was opened. No loose, white arsenic was left.

A few experiments made with this furnace using pure phosgene mixed with air gave a condensate containing very little water and iron, showing that a much purer product could be made by purifying and drying the tail gas before introducing it into the furnace.

SUMMARY AND EXTENSION

1—Arsenic trichloride can be prepared from white arsenic and phosgene at temperatures above 175° C. in the presence of carbon, which acts as a catalyzer.

2—This reaction has been successfully carried out at 200° to 260° C., using pure phosgene in a glass apparatus, and impure "tail gas" from phosgene manufacture in a small scale works apparatus built of iron pipe. The yields were almost quantitative. The product made in the laboratory was water-white and pure except for dissolved phosgene. The condensate from the works apparatus separated into two layers—water, and arsenic trichloride—which contained a small amount of iron in addition to dissolved phosgene. Some arsenic trichloride was lost in the water layer, but preliminary purification of the tail-gas would materially reduce this loss.

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[1] The solubility of phosgene in arsenic trichloride was determined by R. E. Hall and N. W. Rakestraw, of the Edgewood Arsenal Chemical Laboratory.

[1] By a method developed at the Edgewood Arsenal Chemical Laboratory by J. A. Wilkinson and W. T. Schrenk.

3—The method of chlorination used in this work, namely, the treatment of inorganic compounds with phosgene in the presence of carbon as a catalyzer, will probably be of general application, and may make it possible to satisfactorily chlorinate inorganic compounds with phosgene at lower temperatures than has heretofore been possible. Commercially, a number of different types of furnaces, intermittent or continuous, could be used for these reactions:

ACKNOWLEDGMENT

In conclusion it is desired to express appreciation of the kind assistance and suggestions from Major W. L. Evans, of the Edgewood Arsenal Chemical Laboratory, and Majors F. C. Frary and Sterling Temple, of the Edgewood Arsenal Chemical Plants.

THE CHEMICAL INDUSTRY AND TRADE OF SPAIN

By O. P. Hopkins, Washington, D. C.

Received February 2, 1920

The wealth of Spain lies chiefly in her agriculture and in her mineral resources. Of the products that may be called agricultural, and which enter into trade, the best known examples are olive oil, wines, citrus fruits, and nuts. The minerals recovered in the most important quantities are iron, coal, copper, iron pyrites, lead, mercury, zinc, and salt. Cotton textiles are the outstanding product of industrial manufacture.

Although one of the oldest nations in Europe, the Spanish people have not made great progress in developing their resources. At the time the war broke out the domestic production of food was insufficient to meet the home demand coal was largely imported from England while the domestic supply was much neglected, metallic ores were shipped out of the country in immense quantities for others to refine and work, the water power was utilized to only a limited extent, fertilizers were imported ready-made, and so on. Much of the olive oil and wines exported required further refining and blending. Only a few really finished products were shipped out of the country.

In spite of its many disadvantages to Spain, the war has served to change these conditions rather radically. Attention has been focused on the necessity of producing more food at home, for rations were short while hostilities were on. Even olive oil exports were taboo part of the time. The importance of fertilizers is now recognized, and steps have been taken to increase the domestic output, especially of ammonium sulfate. Enough Spanish coal is mined to meet home demands, which run about 7,000,000 tons a year. The developments in mining and metallurgical fields have been more striking than in any other, under the direct stimulus of war demands, and it is considered certain that from now on more and more minerals will be recovered and a much larger percentage refined in Spain.

Special attention has of late been given to hydroelectric development, for which there is considered to be a great future. In 1918 more than 400,000 horsepower was produced by plants having a potential capacity of nearly a million horse power. It is planned to utilize such power more largely in the future for the production of needed alkalies and ammonium sulfate, and in the metallurgical industries.

Trade between the United States and Spain before the war was not comparatively important, and few articles were involved that can be classified as chemical or allied products. It was largely a matter of exchanging American cotton, with some tobacco, mineral oil, electrical equipment, and lumber, for Spanish copper, cork, pyrites, fruits, nuts, and olive oil. The war hindered rather than helped trade, but the enrichment of Spain through the war will probably mean larger purchases from the United States, and, in the end, larger sales to us.

The statistics prepared for this article will show the point to which Spanish chemical industries and trade had developed when the war came and the manner in which the war affected them.

PRODUCTION OF CHEMICALS AND ALLIED PRODUCTS

Official statistics of production are concerned almost exclusively with products of mineral origin. To present a more complete picture of the industries, therefore, some notes have been prepared from various reliable sources, chiefly from material published by the Bureau of Foreign and Domestic Commerce, as follows:

Extensive deposits of potash were discovered as long ago as 1911 in Catalonia, but no definite action was taken toward working them until December 1918, when the government announced conditions under which concessions would be made. A number of explanations are offered to account for the delay in starting production, and charges are made from some quarters that the German syndicate was successful for many years in delaying operations. The government now has entire control of the situation. The first concession was granted to a Belgian company, and an American company has also entered the field. There are no figures of production available.

The manufacture of licorice extract and paste is an important Spanish industry, but there are no statistics of production. This is a comparatively new industry, as formerly the root was exported unmanufactured. Over 6,000,000 lbs. of the root were exported in 1918 and more than 600,000 lbs. of extract and paste.

Before the war about 1,500 tons of benzol were produced in Spain. In 1918, 2,000 tons were produced, and the output for 1919 is estimated at 3,000 tons. This is said to be about one-tenth of the requirements for automobiles alone, and there is keen interest in developing the industry further.

Ferromolybdenum and ferrovanadium are to be manufactured by a new electrochemical company which also plans to produce ferrosilicon and molybdic, tungstic, and vanadic acids, and derivatives and by-products.

Spain is an important producer of a number of essential oils, including spike, rosemary, thyme, sage, pennyroyal, and geranium rose. The plants grow wild and distillation is carried on by large steam distilleries as well as by many small direct-fire stills.

Paints are not manufactured on a large scale in Spain, most of the supplies coming from other countries, the chief of which are shown in the table of imports.

The argols and lees obtained in such large quantities in connection with the extensive production of wine, were formerly exported in the crude state, but the export figures show a tendency to ship the refined products, cream of tartar and calcium tartrate. It is said that tartaric acid is not manufactured in the country.

Ergot of rye was produced to the extent of some 30 tons in 1917, but in 1918 the output was only 5 or 6 tons. Before the war this material was shipped to Germany, but of late it has been going to the United States and England.

The Spanish glass industry is an old one, and exports by quantity are larger than imports. During the war real progress has been made in producing optical and laboratory glass, supplies of which were cut off when hostilities began. The government has placed orders with a successful company and a quantity has been exported.

Spain produces more paper than is required at home, so that there is a considerable export trade. After the war started, and before shipping difficulties became insurmountable, this export trade increased, but later it was seriously interfered with. Supplies of pulp and chemicals from the usual European sources were largely cut down. Ordinary roll paper was formerly produced to the extent of 50,000 metric tons a year, leaving a surplus of some 15,000 tons for export. The output of fine and medium fine papers is estimated at 27,000 metric tons, of which some is exported. The vellum grade is turned out at the rate of about 1,500 reams a day. The value of the vellum paper and bristol board is put at $1,350,000 a year, of which about 20 per cent is exported. Cigarette paper is also manufactured and exported. There are no official statistics of production, the foregoing estimates originating with the American vice-consul at Barcelona. For some time to come there will be a market in Spain for the finer grades of paper, which in the past have been obtained almost exclusively from European sources. The great handicap to the further development of the domestic industry is the necessity of importing pulp, and as the forest resources are unequal to supplying the material, hope is placed in the possibility of developing the esparto production to a point that will make the Spanish paper industry independent.

The foregoing notes are supplementary to the following official production statistics, and can be amplified by a study of the import and export tables. The production table has been compiled from statistics published by the Spanish Ministry of Public Instruction and Fine Arts.

PRODUCTION OF CHEMICALS AND ALLIED PRODUCTS

	QUANTITY PRODUCED	
	1913	1916
CHEMICALS, COLORS, ETC.:	Lbs.	Lbs.
Alcohol, denatured	.....	719,712[1]
Ammonium sulfate	.....	3,284,900
Calcium carbide	.....	34,521,750[2]
Chloride of lime	.....	8,983,800
Copper sulfate	.....	16,755,100
Magnesium carbonate	2,112,000	5,511,600
Hydrochloric acid	.....	2,513,300
Ocher	1,322,800	1,763,700
Olive oil	585,155,300	456,610,300
Potassium chlorate	.....	335,100
Soda:		
Caustic	.....	42,857,900
Chlorate	.....	335,100
Sulfate	646,000	26,477,500
Sulfur:		
Crude	138,126,200	103,447,500
Refined	16,532,500	23,432,900
Sulfuric acid	58,905,300	310,382,100
Superphosphates	.....	694,846,200
ORES, METALS, ETC.:	Metric Tons	Metric Tons
Aluminous earths	388	256
Amblygonite	.....	50
Antimony	.....	515
Argil	6,250	6,302
Asphalt	5,695	2,591
Rock	.....	7,316
Baryta	3,048	10,507
Bismuth	56	10
Briquettes, coal	486,228	555,975
Cement	511,961	536,346
China clay (kaolin)	5,263	1,500
Coal	4,292,522	5,588,668
Coke	595,677	.....
Copper:		
Blister, ingots, wire	23,988	20,768
Matte	7,260	12,111
Ore	2,268,691	1,773,921
Explosives	.....	117,007,681
Fluorspar	351	277
Gas	.....	656,951,604[3]
Gold	.....	376
Graphite	.....	1,240
Iron:		
Ore	9,861,668	5,856,861
Pyrites	926,913	953,678
and Steel	666,769	711,746
Lead:	198,829	147,406
Ore	302,678	267,652
Manganese	21,594	14,178
Mercury	1,246	795
Ore	19,960	19,799
Phosphorite	3,548	14,111
Salt, common	60,429	895,928
Silver:		
Crude	402	274
Fine	125	141
Steatite	4,407	3,561
Tin ore	6,626	86
Wolfram	235	454
Zinc:		
Ore	117,831	166,053
Pigs	3,312	8,523
Sheets	2,691	

[1] Gallons. [2] 1915. [3] Cu. ft., 1915.

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS

As an importer of chemicals and allied products, Spain takes large quantities of fertilizers and insecticides for her agricultural districts, dyes for her cotton-textile industry, and various chemicals for her growing metallurgical industry and the paper and glass industries. Most of the medicines and finer chemical products required for individual consumption are also imported. Very little in these lines has been purchased from the United States in the past, as the market is conveniently situated for German, English, and French manufacturers. During the war, American products have been introduced, in rather small quantities in most cases, although American dyes are now used to a considerable extent. It is possible that this business can be retained in part and perhaps new business gained in some lines, but so much depends upon the outcome of the present political and commercial situation in Europe, that speculation as to the future is almost a waste of time. It will be seen in the following table that imports were greatly interfered with by the war.

The import statistics have been compiled from returns published by the Spanish Department of Customs.

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS

	1913 Lbs.	1916 Lbs.	1918 Lbs.
CHEMICALS, DRUGS, MEDICINES:			
Acetate of lime and pyrolignite of iron	1,460,680	1,106,564	219,790
France	157,021	.....	.....
Germany	4,140	82	.....
United States	1,298,893	1,106,482	.....
Acids:			
Acetic and pyroligneous	10,661	17,742	271
France	3,662	1,656	....
Germany	2,405	.....	...
United Kingdom	1,382	670	.....
United States	.....	15,416	.....
Citric and tartaric acids; alkaline and other citrates and tartrates	956,876	936,862	700,453
France	313,031	484,606	.....
Germany	175,389	785	.....
Italy	187,304	162,437	....
United Kingdom	185,808	252,905	...
United States	.....	36,129	.....
Hydrochloric and sulfuric acids	1,014,147	64,604	17,489
Belgium	415,782	.....	.....
France	310,619	22,306	....
Germany	244,962	49	.....
United Kingdom	26,499	19,914	....
United States	2,176	22,335	...
Nitric acid	59,943	18,060	5,082
France	16,219	1,649	...
Germany	27,920	.....	.....
United Kingdom	12,727	15,549	..
United States	4	862	..
Carbolic acid, naphthalene, creolin, and other similar antiseptics	199,258	213,460	263,168
Belgium	60,240	.....	.....
France	12,919	36,501	.....
Germany	105,510	1,168	....
United Kingdom	3,188	45,007	..
United States	3,940	130,731	...
Sulfoleic and similar acids	85,737	7,824	...
France	65,803	.....	.
Germany	17,551	.....	.....
United Kingdom	.....	7,824	..
Albumin	58,043	59,643	66,419
China	9,744	18,900	.....
France	20,928	27,817	.....
Germany	17,209	.....	.....
United Kingdom	4,343	12,926	...
Alkaline carbonates, borates, silicates; salts of ammonia (except sulfate)	10,186,839	4,977,273	2,636,607
Belgium	1,034,297	.....	.....
France	2,108,301	347,833	.....
Germany	952,081	32,822	.....
United Kingdom	5,569,761	4,241,919	...
United States	.....	58,801	...
Alkaloids, other than quinine, and their salts	2,332	4,440	6,512
France	813	1,982	....
Germany	1,491	57	..
Switzerland	.....	1,156	...
United Kingdom	24	1,199	..
United States	.....	46	...
Alums, sulfate, chloride, and acetate of alumina, aluminate of soda, sulfate of magnesia, and kieserite	1,034,460	2,329,898	553,056
France	415,369	641,424	.....
Germany	359,976	2,218	...
United Kingdom	177,816	1,555,301	....
United States	.....	19,733	....
Antipyrin and similar products	4,204	17,910	21,383
France	1,512	5,044	.
Germany	2,595	1,155	....
Switzerland	20	3,787	..
United Kingdom	53	3,316	....
United States	.....	3,208	.
Calcium carbide	106,744	3,413	23,360
France	105,465	3,373	.
Germany	825	.....	..
CHEMICALS, DRUGS, ETC. (*Continued*)			
Chemical products, n. e. s.	8,653,095	6,305,182	2,911,737
Belgium	829,838	.....	.....
France	1,803,607	1,736,492	.....
Germany	3,856,889	407,939	.....
Netherlands	352,294	246,379	.....
United Kingdom	918,632	1,627,177	.....
United States	126,619	1,854,236	.....
Chloride of lime	8,551,431	1,130,455	2,179,578
France	8,006,256	16,735	.....
United Kingdom	320,944	558,193	.....
United States	.....	438,022	.....
Chloroform	2,579	6,314	9,520
France	1,007	3,440	.....
United Kingdom	1,128	2,676	....
United States	.....	198	.....
Ether	23,065	7,484	2,749
France	4,892	3,130	.....
Germany	17,715	.....	.....
Switzerland	.....	4,103	.....
Fertilizers:			
Superphosphate and Thomas slag	331,208,502	50,831,378	24,390
Belgium	61,667,139	.....	.....
France	113,968,523	16,603,282	....
Germany	33,673,751	.....	.....
Netherlands	53,476,932	.....	....
Portugal	36,516,046	34,228,096	.....
United Kingdom	31,805,466	.....	...
Nitrate of soda	73,270,864	98,614,242	41,337,866
Belgium	3,790,702	.....	.....
Chile	51,160,862	85,589,966	....
France	2,668,516	60,979	.....
Germany	5,776,138	881,840	.....
Portugal	....	4,042,059	.....
United Kingdom	9,495,675	1,753,788	...
United States	.....	6,276,792	.
Other; sulfate of ammonia; potash salts (except kieserite	203,315,445	139,548,051	270,584
Belgium	9,175,455	.....	.....
Chile	1,392,652	1,580,764	.....
France	8,979,448	127,741	.....
Germany	55,917,984	4,674	.....
Norway	2,100,102	.....	.....
Portugal	9,480	1,769,233	.....
Russia	8,299,422	.....	.....
United Kingdom	117,046,092	135,875,309	.....
United States	.....	95,300	.....
	Metric tons	Metric tons	Metric tons
Phosphate rock	244,463	288,328	115,028
Algeria	122,375	163,360	.....
Tunis	16,372	24,203	.....
France and Colonies	28,374	22,900	....
United States	69,387	70,638	.....
	Lbs.	Lbs.	Lbs.
Gelatin for industrial purposes	275,540	146,892	54,992
France	153,393	102,494	.....
Switzerland	29,208	12,324	....
United Kingdom	14,667	23,618	.....
United States	.....	1,082	..
Glycerin	192,138	2,399	68
France	24,286	1,782	...
Germany	52,751	.....	..
Netherlands	102,878	.....	..
United Kingdom	9,760	498	..
United States	....	119	...
Insecticides, including sulfates of copper and iron, and cyanides of potassium and sodium	14,178,750	8,908,909	348,934
France	1,252,350	568,520	...
Germany	703,512	....	..
United Kingdom	11,992,850	976,059	...
United States	522	6,631,131	.
Lead oxides	375,357	33,854	33,653
France	37,718	8,993	..
Germany	250,143	...	...
Morocco	.....	12,035	..
Netherlands	52,714	..	..
United Kingdom	32,767	10,615	...
United States	.....	2,211	...
Licorice extract	44,443	7,529	392
Medicines:			
Containing sugar, glucose, saccharin, etc., without alcohol	73,345	50,122	51,610
France	60,466	34,330	...
United Kingdom	7,052	8,578	...
United States	2,540	4,111	....
Containing alcohol, n. s. m	16,027	22,968	32,373
France	13,023	14,742	...
Germany	1,788	22	..
Switzerland	24	3,005	..
United Kingdom	46	4,006	.
United States	972	970	..
Perfumes:			
Alcoholic	101,915	93,540	82,900
Other, and essential oils	338,526	372,643	500,967
Pharmaceutical products, n. s. m.	615,231	634,301	757,687
France	322,070	412,586	
Germany	135,832	5,132	
United Kingdom	80,602	101,236	.
United States	43,628	53,598	
Phosphorus	53,825	48,192	4,630
France	23,704	2,205	.
United Kingdom	30,121	43,782	.....

Imports of Chemicals and Allied Products (*Continued*)

Articles	1913 Lbs.	1916 Lbs.	1918 Lbs.
Chemicals, Drugs, Etc. (*Continued*)			
Pills, capsules, pellets, for medicinal use	60,524	41,698	39,075
France	37,134	30,746	.....
Germany	9,841	13	.....
United Kingdom	2,575	2,582	.....
United States	10,527	6,827	.....
Potassium and sodium chlorates and phosphoric acid	133,054	212,279	101,388
France	56,724	83,950	.....
Sweden	24,386	.....	.....
Switzerland	.....	42,734	.....
United Kingdom	41,318	57,955	.....
United States	.....	3,549	.....
Quinine, and salts	10,668	11,539	8,508
France	4,738	5,653	.....
Germany	3,479	7	.....
United Kingdom	368	1,692	.....
United States	850	701	.....
Soda:			
Caustic, and caustic potash	366,746	46,665	4,989
Belgium	104,630	.....	.....
Germany	97,916	260	.....
United Kingdom	151,758	33,000	.....
United States	.....	6,329	.....
Chloride	9,426,030	298,673	29,445
France	262,910	167,726	.....
Portugal	8,983,393	3,086	.....
United Kingdom	175,226	127,682	.....
United States	3,106	179	.....
Sulfate and sulfite; chloride and carbonate of magnesia	9,158,702	2,557,873	1,521,820
Belgium	592,846	.....	.....
France	784,130	673,003	.....
Germany	1,755,382	54,610	.....
United Kingdom	5,577,858	1,020,068	.....
United States	869	513,797	.....
Saccharin and similar products	333	15	.....
Sulfur:			
Crude, not ground	4,798,109	3,945,800	.....
France	36,398	1,219,773	.....
Italy	4,708,403	2,726,027	.....
Refined, not ground	2,708,094	4,349,285	2,609,318
France	59,864	1,016,584	.....
Italy	2,555,633	3,285,610	.....
Refined, ground; flowers of sulfur	15,413,332	17,723,065	6,707,213
France	1,753,195	4,126,550	.....
Italy	13,302,823	13,445,156	.....
Tannin	60,794	37,143	5,121
France	21,349	9,802	.....
Germany	39,004	.....	.....
United Kingdom	.....	27,050	.....
Dyes and Dyestuffs:			
Aniline oil and muriate	1,141,169	879,033	1,572,627
France	191,110	796	.....
Germany	809,007	1,572	.....
United Kingdom	141,052	1,700	.....
United States	.....	874,780	.....
Artificial, in paste or liquid	84,840	75,807	102,166
France	15,190	16,311	.....
Germany	58,415	12,379	.....
Switzerland	7,397	44,630	.....
Coal-tar dyes and other artificial dyes, in powder or crystals	1,264,062	444,624	850,523
France	81,328	31,845	.....
Germany	1,085,135	192,154	.....
Switzerland	71,321	119,004	.....
United States	198	51,735	.....
Indigo, natural or synthetic; cochineal	167,561	485,614	929,246
Canary Islands	2,416	113,341	.....
Germany	155,327	316,164	.....
Switzerland	3,286	39,370	.....
Thio-carbon	681,254	74,057	397,996
France	20,593	.....	.....
Germany	598,794	36,462	.....
Switzerland	27,136	26,592	.....
United States	.....	11,003	.....
Vegetable extracts for dyeing, liquid or solid, including garancine	11,827,124	7,469,965	2,352,987
Argentina	2,103,764	3,963,082	.....
British Possessions	979,927	383,077	.....
France	4,608,064	938,536	.....
Germany	752,426	547	.....
Italy	2,488,449	.....	.....
Switzerland	81,239	41,427	.....
United Kingdom	569,381	779,273	.....
United States	61,100	1,282,667	.....
Paints, Pigments, Colors, Etc.:			
Ochers and coloring earths for painting, unground, and alumina in powder	2,085,291	72,844	26,643
France	35,428	39,683	.....
Germany	1,420,721	.....	.....
United Kingdom	24,524	33,152	.....
Ochers and coloring earths, ground	2,427,646	1,869,364	131,625
France	1,185,151	1,337,604	.....
Germany	717,990	5,714	.....
Switzerland	.....	24,251	.....
United Kingdom	430,664	483,590	.....
Mineral colors and colors prepared with water	6,805,435	2,383,819	1,435,013
Belgium	994,237	.....	.....
France	1,668,849	1,250,478	.....

Imports of Chemicals and Allied Products (*Concluded*)

	1913 Lbs.	1916 Lbs.	1918 Lbs.
Paints, Pigments, Etc. (*Concluded*)			
Mineral colors, etc. (*Concluded*)			
Germany	2,852,148	27,668	.....
Netherlands	557,861	64,762	.....
United Kingdom	565,063	954,528	.....
United States	84,280	67,827	.....
Colors prepared with oils, varnish, glue, etc., liquid, in paste, or solid	2,248,624	1,886,254	1,009,590
France	261,023	274,768	.....
Germany	545,008	2,425	.....
Netherlands	74,762	154,942	.....
United Kingdom	1,149,066	1,228,516	.....
United States	133,879	203,042	.....
Inks:			
Writing	319,764	163,068	111,481
France	84,802	51,105	.....
Germany	150,997	.....	.....
Netherlands	1,548	31,059	.....
United Kingdom	69,756	76,150	.....
United States	11,151	4,528	.....
Printing; shoe creams and polishes	1,518,171	709,597	454,227
Belgium	244,702	.....	.....
France	206,961	270,394	.....
Germany	841,405	.....	.....
Italy	1,362	88,239	.....
United Kingdom	82,997	134,136	.....
United States	99,886	205,169	.....
Varnishes:			
Containing alcohol	57,117	45,637	17,317
France	33,512	29,310	.....
United Kingdom	15,409	14,694	.....
United States	.....	1,633	.....
Other	1,415,170	1,170,601	300,796
Belgium	135,779	.....	.....
France	256,980	171,240	.....
Germany	168,156	.....	.....
Netherlands	68,682	73,030	.....
United Kingdom	718,124	808,206	.....
United States	64,833	114,800	.....
Oils, Oilseeds, Fats and Waxes:			
Coconut and palm oil, other solid oils, and olein	2,299,635	2,638,168	572,981
France	888,297	996,443	.....
United Kingdom	796,395	618,727	.....
Other vegetable oils (except olive oil)	1,030,826	205,495	1,031,045
Belgium	230,778	.....	.....
France	457,190	38,488	.....
United Kingdom	192,682	110,130	.....
	Metric tons	Metric tons	Metric tons
Sesame, linseed, and other oilseeds, including copra	70,848	44,870	16,104
Argentina	25	10,748	.....
British Possessions in Asia	35,906	11,534	.....
China	4,745	2,232	.....
Dutch East Indies	15,781	3,528	.....
Philippines	11,168	11,689	.....
	Lbs.	Lbs	Lbs.
Paraffin	11,904,378	14,671,750	2,523,984
Stearin and palmitin	503,439	16,700	4,429
Belgium	128,144	.....	.....
Germany	188,323	.....	.....
United States	1,351	11,310	.....
Wax:			
Animal	45,501	20,221	423,667
Mineral and vegetable	681,305	224,819	139,411
Miscellaneous Materials and Products:			
Animal products used in medicine	414,293	99,920	93,286
Barks and woods for dyeing and tanning	559,275	19,331,465	7,190,385
Bone-black	419,844	138,050	113,170
Caramel, liquid, and similar products	32,695	8,126	13
Colophony, vegetable pitch, etc.	682,683	374,885	197,975
Glass and glassware	13,121,606	4,271,190	2,360,663
Glucose	725	2,400	9,190
Glue	1,664,167	330,641	205,300
France	573,322	247,885	.....
United Kingdom	554,856	42,352	.....
United States	11,823	20,470	.....
Paper and manufactures	10,191,180	4,571,086	4,694,075
Paper pulp	134,352,733	151,125,330	71,462,109
Prepared size, dextrin, etc.	3,726,210	1,815,755	77,212
Germany	1,754,300	.....	.....
Holland	1,332,963	897,280	.....
United Kingdom	151,259	657,412	.....
United States	.....	189,700	.....
Soap, common	796,620	308,605	763,328
Sugar	81,948	40,412,207	33,497,513
Vegetable products used in medicine	490,160	285.783	215.488

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS

Not many chemicals are exported by Spain, although the quantities have been increasing under the stimulus of high prices. Among the exports, however, are a number of extremely important materials for the chemical industries of other countries, as the following table will show. These figures have been compiled from statistics issued by the Spanish Department of Customs.

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS

	1913	1916	1918
	Lbs.	Lbs.	Lbs.
CHEMICALS, DRUGS, MEDICINES:			
Chemical products, n e. s.	3,037,265	70,123,194	40,249,587
France	41,625	50,257,512	.....
Germany	987,985	.....	.....
Portugal	96,3[illegible]	9,031,828	.....
United Kingdom	938,314	1,742,494	.....
Chloride of lime	419,552	1,170,725	105,116
Portugal	391,982	955,208	.....
Copper sulfate	4,546	43,905	250,004
Egypt	.....	43,541	.....
France	4,546	.....	.....
Glycerin	3,345,487	1,860,898	1,993,224
France	714,183	...	.....
Italy	.....	172,481	.....
United States	1,016,720	1,508,903	.....
Licorice:			
Crude	4,570,227	6,780,737	6,130,352
France	1,848,250	3,361,705	.....
Portugal	520,745	5,560	.....
United States	1,565,518	3,084,222	.....
Extract and paste	930,792	1,328,680	606,230
France	385,075	403,228	.....
United States	505,992	689,811	.....
Perfumes and essential oils	433,475	1,012,612	1,280,017
Pharmaceutical products, n. e. s.	972,954	1,547,777	2,321,680
Argentina	220,612	186,608	.....
Italy	15,851	144,092	.....
Morocco	20,734	331,705	.....
Salts, mineral, n. e. s.	2,670	10,400	2,405,227
Soda:			
Caustic	230,557	5,990,546	8,037,639
Netherlands	225,797	.....	.....
Portugal	68	5,552,896	.....
	Metric tons	Metric tons	Metric tons
Chloride	564,041	423,035	336,068
British Possessions in America	69,740	84,528	.....
British Possessions in Asia	78,012	96,889	.....
Uruguay	120,241	56,755	.....
	Lbs.	Lbs.	Lbs.
Sulfate	.....	696,262	419,685
Egypt	.....	166,449	.....
Italy	.....	485,017	.....
Sulfur	4,868	1,243	559,123
Tartar:			
Crude	27,739,557	16,338,750	10,965,288
France	14,101,625	5,284,230	.....
Italy	125,976	2,891,329	.....
Netherlands	7,267,246	.....	.....
United Kingdom	4,506,800	5,278,452	.....
United States	293,706	2,826,672	.....
Cream of	.....	701,154	1,161,382
Denmark	.....	85,964	.....
United Kingdom	.....	546,570	.....
Tartrate of lime	1,487,695	1,470,150	2,654,749
France	333,553	.....	.....
Italy	216,315	48,034	.....
Netherlands	477,845	.....	.....
United Kingdom	248,245	1,126,860	.....
United States	.....	295,256	.....
PAINTS, PIGMENTS, COLORS, VARNISHES:			
Colors, in lumps or powder	293,792	3,148,868	4,855,400
France	16,219	2,495,004	.....
Germany	112,621	.....	.....
Cuba	55,795	137,237	.....
Morocco	32,512	25,139	.....
Colors, prepared for painting	530,475	2,389,170	918,744
Argentina	331,081	191,295	.....
France	1,127	1,386,712	.....
United States	.....	203,180	.....
Uruguay	106,688	89,586	.....
Minimum	178,504	434,340	623,038
Ochers and coloring earths	3,269,315	3,114,228	2,563,375
France	581,526	160,011	.....
Germany	447,521	.....	.....
United Kingdom	1,598,587	2,718,850	.....
Varnishes	3,759	21,024	54,768
Argentina	992	441	.....
Canary Islands	1,750	309	.....
France	.....	9,100	.....
Italy	.....	5,904	.....
OILS, OILSEEDS, FATS AND WAXES:			
Almond oil	7,961	1,733	386
Peanut oil	18,435	.....	168
Oil of other seeds	35,576	1,313,957	3,582,313
Residuum of olive oil	240,233	1,081,860	.....
Peanuts	11,827,380	7,160,404	2,294,360
Stearin	24,683	654,103	92,268
Wax	45,589	199,016	456,584
ORES:	Metric tons	Metric tons	Metric toos
Antimony	20	53	.....
Roumania	.....	20	.....
Switzerland	.....	15	.....
United Kingdom	20	.....	.....
Blende	91,610	58,634	47,666
Belgium	53,280	.....	.....
France	19,510	7,793	.....
ORES (*Concluded*)			
Blende (*Concluded*)			
Germany	10,300	.....	....
United Kingdom	3,895	6,714	.....
United States	.....	40,959	.....
Calamine:			
Crude	12,367	40,898	1,200
Belgium	10,908	.....	.....
Netherlands	550	37,689	.....
Calcined	10,442	.....	5,295
Belgium	6,592	.....	.....
France	3,850	.....	.....
Copper:			
Ores over $2\frac{1}{2}$ per cent	86,091	22,461	5,257
Germany	9,452	.....	.....
Netherlands	10,390	.....	.....
United Kingdom	38,196	18,181	.....
United States	19,108	4,261	.....
Ores under $2\frac{1}{2}$ per cent	74,294	23,145	17,093
France	15,628	.....	.....
United Kingdom	41,152	23,145	.....
Matte	214	.....	.....
Belgium	214	.....	.....
Galena:			
Silver-bearing	942	255	46
Belgium	941	.....	.....
France	.....	255	.....
Other than silver-bearing	1,147	976	67
Belgium	228	.....	.....
France	789	801	.....
Iron:			
Ores	8,907,309	5,045,575	4,292,406
France	390,073	407,019	.....
Germany	987,626	.....	.....
Netherlands	2,510,694	108	.....
United Kingdom	4,818,617	4,521,013	.....
United States	89,828	116,793	.....
Pyrites	2,903,554	2,744,767	1,065,701
France	383,605	613,069	.....
Germany	458,655	.....	.....
Netherlands	521,669	48,039	.....
United Kingdom	548,319	859,374	.....
United States	705,733	1,141,981	.....
Lead ores, n. e. s.	260	730	374
Manganese ores	27,793	8,851	22,521
Belgium	23,014	.....	.....
France	537	5,767	.....
United Kingdom	4,128	2,472	.....
Ores, n. e. s	285	1,741	500
France	141	160	.....
Italy	10	1,171	.....
Phosphorite	.....	.....	600
MISCELLANEOUS MATERIALS AND PRODUCTS:	Lbs.	Lbs	Lbs.
Barks and other tanning materials	6,110,539	24,843,128	12,546,830
Candles:			
Stearin	744,754	827,538	96,294
Wax	45,589	115,372	754,924
Explosives	30,675	294,734	647,620
Glass:			
Hollow, common	16,487,305	24,508,248	14,355,970
Argentina	.....	3,240,268	.....
Cuba	3,146,344	5,412,646	.....
France	537,264	11,278,956	.....
All other	345,863	5,604,566	5,076,760
Glue, common	17,465	323,026	525,082
Belgium	11,023	.....	.....
United Kingdom	661	291,396	.....
Naval stores:			
Rosin	18,328,503	23,662,849	11,786,960
Belgium	9,119,354	.....	.....
Germany	1,311,386	.....	.....
Italy	13,118	5,696,960	.....
Portugal	1,210,077	1,359,233	.....
United Kingdom	5,797,343	16,066,370	.....
Turpentine	9,571,064	8,234,308	5,113,364
Belgium	2,727,118	.....	.....
France	5,664,594	1,380,285	.....
Italy	.....	1,600,983	.....
United Kingdom	263,435	5,077,547	....
Paper:			
Total exports	17,446,544	40,807,525	18,401,808
Cigarette	4,022,863	5,564,872	7,553,962
Chile	165,428	560,673	....
Cuba	1,628,600	1,276,470	.....
Mexico	983,559	489,110	.....
Hand-made	1,471,720	763,148	272,033
Argentina	705,812	371,849	.....
In rolls	1,542,508	13,246,300	220,039
Belgium	596,551	.....	....
France	....	11,823,198	.....
Netherlands	308,010	44,538	....
United Kingdom	522	436,244	....
Other; cardboard; manufactures of paper and cardboard	10,409,453	21,233,205	10,355,774
Soap, common	4,202,650	7,824,560	8,700,910
Cuba	3,450,474	3,567,692	.....
France	639	1,621,482	.....
United Kingdom	78,462	729,743	.....
United States	126,446	521,054	.....
Sugar	23,274	5,579,425	1,390,300
Argentina	21,982	78,970	.....
Canary Islands	.....	1,473,880	.....
Portugal	330	3,112,995	...
Vegitable pitch	180,294	212,435	1,466,867

ORIGINAL PAPERS

CATALYTIC OXIDATION. I—BENZENE[1]

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PRELIMINARY COMMUNICATION

The present communication is for the most part preliminary and is essentially an announcement of results obtained in a new and hitherto substantially untouched field of organic chemistry involving novel reactions and the production commercially of products which have previously been considered as laboratory curiosities of purely theoretical interest. The facts established also seem to throw some doubt on the theories of catalytic action which have been accepted in the past, but it is not our intention to enter into a discussion of this aspect at the present time but to reserve these considerations for a later communication when certain experimental work on the theoretical side of catalytic oxidation has been completed. The literature regarding catalytic oxidation in general is very extensive, but that portion bearing specifically on the oxidation of benzene short of complete combustion is quite meagre.

In 1870, Carius[2] formed the so-called "trichlorophenomalonic acid" (chloromaleic acid) by treating benzene with "hydrated chloric acid" (free perchloric acid generated by the treatment of potassium chlorate with sulfuric acid). Coquillon,[3] in 1875, stated that both benzene and toluene gave benzaldehyde and benzoic acid when the vapor of the hydrocarbon and air were passed through a tube containing incandescent platinum wire. These products noted from benzene were possibly due to toluene present as an impurity in the benzene. A little later Kekulé and Strecker[1] repeated the experiments of Carius[5] in connection with their classic work on the constitution of the benzene molecule and found that the trichlorophenomalonic acid was converted by warm baryta water into maleic acid.

The first really important article in this field was that of Walter,[6] in which was described the air oxidation of toluene to benzoic acid and benzaldehyde and of anthracene to anthraquinone using vanadium oxide as a catalyzer. Later, in 1904 and 1905, German, French and British patents[7] were taken out covering the processes disclosed in the paper. In the patents a whole series of catalyzers were listed and besides the reactions mentioned above, Walter claimed the production of acetic acid and aldehyde from alcohol, carbazol from diphenylamine, diphenyl from benzene, β-naphthol from naphthalene, and various unidentified products from petroleum oils. The work of Walter, however, was largely qualitative and the control of conditions such that, except for the hints of possibilities, the articles and patents are of little practical value.

Zincke[1] obtained dichloromaleic acid by the action of chlorine on *p*-aminophenol in alkaline solution. Derivatives of heterocyclic ring compounds such as furfurane, thiophene and pyrrole, according to Ciamician and Silber,[2] and Ciamician and Angeli,[3] likewise yield derivatives of maleic acid. A British patent[4] to Wedge claims the production of phenol from liquid benzene by oxidation with ozone or ozonized air in the presence of catalysts such as platinum black. Kempf[5] in a paper dealing largely with theoretical consideration of the constitution of the benzene molecule notes the formation of maleic acid by the liquid phase oxidation of benzoquinone with peroxide of silver.

In 1907, however, the most important and most thorough researches on catalytic oxidation of organic compounds began to appear. The work of Orloff[6] is of extreme value both for the data given and for the theoretical considerations presented. He also published a very valuable theoretical article in 1909.[7] Most of this work has been collected into two books.[8] The work of Orloff covered very thoroughly the oxidation of alcohols. His work on hydrocarbons was merely preliminary. He worked mainly on Baku petroleum, but gave some study to benzene and toluene. He produced benzaldehyde from the latter and a number of *unidentified* products from the former using a copper sieve contact mass. He also oxidized turpentine in this manner, but obtained no definite products.

About the same time Woog[9] reports the production of benzaldehyde from toluene in the vapor phase by the action of platinum and other catalysts. In 1908 patents were taken out by the Farbenfabrik v. F. Bayer & Co.,[10] covering the production of methyladipic acid by the liquid phase oxidation, with nitric acid and alkaline potassium permanganate successively, of methylcyclohexanol or methylcyclohexanone, giving another instance of the splitting of the benzene ring without complete oxidation. A later patent[11] to A. Lowenthal covers the oxidation of aromatic hydrocarbons or alcohols to aldehydes in the presence of chromium catalyzers. The patent is very vague and lacking in detail.

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[1] Read before the New York Section of the American Chemical Society, Chemists' Club, New York, N. Y., January 9, 1920.

[2] *Ann.*, **155**, 217–233.

[3] *Compt. rend* , **80**, 1089–90.

[4] *Ann.*, **223** (1884), 170–197; **239**, 176.

[5] *Loc. cit.*

[6] *J. prakt. Chem.*, **1892**, 107–111.

[7] D. R. P. 168,291, Class 120, Oct. 28, 1904, French Patent 360,785, Oct. 11, 1905; Brit. Patent 21,941, Oct. 27, 1905.

[1] *Ber.*, **24** (1891), 912.

[2] *Ibid.*, **20** (1887), 698, 2594.

[3] *Ibid.*, **24** (1891), 77, 1347.

[4] Brit. Patent 2,010, April 20, 1901.

[5] *Ber.*, **39** (1906), 3715–27.

[6] *J. Russ. Phys. Chem. Soc.*, **39** (1907), 855, 1023, 1414; **40** (1908), 652, 659, 796, 799, 1590, 1596.

[7] *Z. physik. Chem.*, **69**, 499–505.

[8] "Der bisherige Stand der wissenshaftlichen Erkentniss und der technischen Verwendung sowie neue Üntersuchungen uber seine Herstellung und uber pyrogenetische Kontactreaktionen," trans. into German, C. Kietaihl Barth, Leipzig, 1909; "Formaldehyd," Barth, Leipzig, 1909.

[9] *Compt. rend.*, **145**, 124–6.

[10] D. R. P. 221,849, Oct. 12, 1908, French Patent 409,083, Nov. 15, 1908; Brit. Patent 24,298, Oct. 22, 1909.

[11] D. R. P. 239,651, June 25, 1909.

Kempf[1] gives a very long and interesting article regarding the liquid phase oxidation of quinone by means of the electric current to form maleic acid. The work is largely theoretical but is of extreme interest in this connection. A German patent[2] to Farbenfabrik v. F. Bayer covers the production of erythrene by the incomplete combustion of many organic substances, among which are mentioned benzene, toluene, and naphthalene. Willstätter and Sonnenfelt[3] describe the production of adipic acid and aldehyde by oxidation of cyclohexanol in the liquid phase in the presence of metals of the platinum group.

Finally, we would mention the work of H. D. Gibbs and his associates at the Bureau of Chemistry on the catalytic oxidation of organic compounds. This work to a great extent paralleled our own and in some instances duplicated it. The Bureau has published little detail of the work but American and foreign patents have appeared on the production of phthalic anhydride from naphthalene, anthraquinone from anthracene, phenanthraquinone from phenanthrene, and benzaldehyde from toluene, using various catalyzers and temperature ranges in the specific processes.[4]

Of our own work in this field which has been carried on over an extended period of time, five U. S. patents and a number of various foreign patents have so far appeared, four of the U. S. patents dealing with the oxidation of benzene in the vapor phase in the presence of a catalyzer. Under varying conditions diphenyl, benzoquinone, or maleic acid have been obtained.

Because of our long standing interest in the disinfectant field we had speculated considerably upon the cause of the formation of the relatively large proportions of tar acids in the so-called Scotch blast-furnace tars. In these furnaces coal, iron ore and air are present and this combination appears to be responsible for the peculiar high tar-acid content of these tars. In this country coke is used almost exclusively in blast furnaces with consequently little or no tar formation. We, therefore, decided to attempt to duplicate these supposed conditions namely, the contact of hydrocarbons, iron oxide and air—by passing tar oil vapors admixed with air through heated tubes filled with iron oxide. A very short time, however, convinced us of the uselessness of working with such complex mixtures and we turned our attention entirely to benzene, which could readily be obtained in the pure state. Later, because of the outbreak of the war, the demand for phenol became very insistent and the problem viewed from the production of this material became of more practical importance than the theoretical considerations concerning the formation of the complex Scotch acids.

For an investigation of the mechanism of the oxidation of benzene to phenol in the vapor phase a study of temperature effects was first in order and we soon found that at the higher temperatures, diphenyl, tarry products and complete combustion were the only results. From these experiments, however, we learned that the presence of steam in moderate amount aided the production of high yields of diphenyl of good quality and, moreover, that increased pressure was favorable to the course of the reaction. These developments are covered in a recent patent[1] taken out by the authors

In some of the work at temperatures below diphenyl formation we had obtained traces of phenols with certain catalysts, so we decided to make an exhaustive investigation of these possibilities. We reviewed the periodic system and determined to try every metal and metallic oxide which would be stable under the conditions of experiment, to determine which, if any, exerted catalytic action. We may say here that we completed this program and in addition tried many mixtures although, of course, we could not exhaust all the possible permutations and combinations of materials and conditions. Wherever a trace of product was formed we went thoroughly into the various combinations with that particular catalyst in attempts to enlarge the observations to commercial possibilities. In no case did we secure yields of phenol at all approaching anything commercial, although in the cases of a few catalysts we obtained conversions of from 0.2 to 0.3 per cent. We did, however, at a very early stage of our investigation produce benzoquinone with a number of catalysts and discovered further that with certain catalysts, notably vanadium oxide, there was a considerable formation (in the initial experiments about 4 per cent) of a highly water-soluble acid which was readily identified as maleic acid. This result was so remarkable that we split our investigation at once into two phases and, continuing one group of men on the general subject of catalytic oxidation, formed another group to take up the production of maleic acid and improve the yields and develop technical apparatus to a point where a commercial process might be possible. The processes involved have been covered in three U. S. patents taken out by the authors.[2]

The investigation of vapor-phase oxidation is exceedingly complex because of the number of factors affecting the reactions, for example, variations in ratio of oxygen to hydrocarbon, catalyst form, pressure conditions, effect of water vapor and fixed gases, catalyst deterioration and revivification, temperature control, time of contact, secondary and by-reactions, etc. Several of these factors, such as temperature control, may be subdivided into a number of problems, each of which may be very difficult of solution especially if it is desired to construct large scale apparatus for the commercial production of the oxidation products. The number of experiments involved was enormous and has required very extended careful work over a long period of time.

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[1] *J. prakt. Chem.*, **83** (1911), 329–94.

[2] D. R. P. 278,647, Class 120, Aug. 5, 1912.

[3] *Ber.*, **46** (1913), 2952–8.

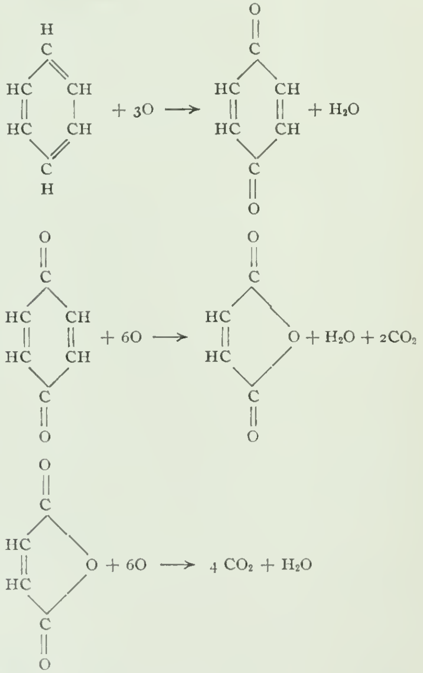
[4] Brit. Patents 14,150, Oct. 1, 1917; 14,151, Oct. 1, 1917. Canadian Patents 186,444, Sept. 10, 1918; 186,445, Sept. 10, 1918. U. S. Patents 1,284,887, Nov 12, 1918; 1,284,888, Nov. 12, 1918; 1,285,117, Nov. 19, 1918; 1,288,431, Dec. 17, 1918; 1,303,168, May 6, 1919.

[1] U. S. Patent 1,322,983, Nov. 25, 1919.

[2] U. S. Patents 1,318,631, 1,318,632, and 1,318,633, all issued Oct. 14, 1919.

Our laboratory work has been carried on with the direct object of solving the problems of commercial application simultaneously with the theoretical aspect of the problem as a whole. We have from the first attempted to perfect a laboratory apparatus which would allow of uniform temperature control, and a description of such an apparatus is given later in this paper. This was absolutely essential as we have found that the problem of temperature control is the most important single difficulty to be solved. This is evident from the following considerations in connection with the oxidation of benzene.

The reactions which we have identified as taking place with such catalysts as molybdenum and vanadium we will consider in step-wise form and are mainly as follows:



That is, during catalytic oxidation of benzene, quinone is first formed, then oxidized to maleic anhydride, and this in turn burned completely to CO_2 and H_2O. The preferred reaction involves a splitting of the benzene nucleus without complete oxidation.

There are, of course, two acids, maleic and fumaric, which are isomeric, but from our experience maleic acid is the primary product obtained during the reaction. This is explainable in that only maleic acid forms an anhydride and this appears to be the stable form at the temperature of the reaction. Some maleic acid is probably always formed as a secondary reaction product due to the hydration of the anhydride during condensation. Small amounts of fumaric acid are usually present in the products because of rearrangement during condensation. Another side reaction is responsible for the formation of definite amounts of formaldehyde but we will not consider the genesis of this compound in the present paper.

The total amount of oxygen needed to completely burn one molecule of benzene is fifteen atoms. It is conceivable that the intermediate products previously mentioned are formed and immediately burned to the more highly oxidized form even in the ordinary combustion of benzene but that they cannot be isolated as such because of the extreme velocity of the combustion reaction. The function of a catalyst, which by its use allows the separation of the intermediate products of combustion, is, of course, problematical, but it would appear that by its presence the range of temperature between the formation of one intermediate product and its combustion to a higher degree of oxidation is broadened, and that, by a close temperature regulation within this range throughout which the intermediate is stable, it may be isolated. Another contact substance which either shows no reaction or produces complete combustion at a higher temperature does not provide this sufficiently broad temperature range and the only products of reaction are those of complete combustion. An example of the former contact substance is vanadium oxide, and examples of the latter are cerium oxide, platinum, and numerous others. Even with these it is possible that sufficiently close regulation will result in the isolation of intermediate products and it is further possible and even probable that in other cases suitable control would make possible the isolation of other products, such as phenol.

It has been mentioned above that the question of temperature control is of extreme importance, and for purposes of comparison we are giving the amount of heat developed during the oxidation of benzene, sulfur dioxide, and ammonia.

In Table I we have collected data from the literature bearing on the subject of benzene oxidation.

The values given for the heat of combustion for quinone and maleic acid are for the solid form of the compound. The heats of combustion in vapor form are therefore somewhat greater since heat must be absorbed in melting and volatilizing the compounds.

From this it is evident that the heat developed in the formation of maleic acid from benzene is nearly 60 per cent of that developed by a benzene flame.

These are, of course, the theoretical values, but as we have not succeeded as yet in producing simple reactions as represented by any of the single equations without the simultaneous production of other reactions, the amount of heat formed is a composite of all the values given above. An inspection of these values reveals the accelerating character of the heat formation which takes place with the increasing degree of oxidation and since the tendency to higher oxidation increases with the temperature for a given set of conditions it is evident that the temperature control must be most refined.

TABLE I—OXIDATION OF BENZENE

	B. t. u. per Lb. of Substance	B. t. u. per Lb. of C_6H_6
I—HEATS OF COMBUSTION		
(1) Benzene: 785.1 kg. cal. per mol.; 10.06 kg. cal. per g	18,108	18,108
(2) Quinone: 654.8 kg. cal. per mol.; 6.06 kg. cal. per g	10,908	15,102
(3) Maleic Acid: 327.0 kg. cal. per mol.; 2.81 kg. cal. per g	5,058	7,542
II—HEATS OF FORMATION (calculated)		
From Benzene		
(1) to Quinone: 130.3 kg. cal. per mol.; 1.21 kg. cal. per g	2,178	3,006
(2) to Maleic Acid: 458.1 kg. cal. per mol.; 3.95 kg. cal. per g	7,110	10,566
From Quinone		
(3) to Maleic Acid: 327.8 kg. cal. per mol.; 2.82 kg. cal. per g	5,076	7,560

SUMMARY	B. t. u. per Lb. C_6H_6
Benzene to quinone	3,006
Quinone to maleic acid	7,560
Maleic acid to complete combustion	7,542
TOTAL	18,108

Benzene: Landolt, p. 910; Berthelot, *Ann. chim. phys.*, [5] **23** (1881), 188.

Quinone: Landolt, p. 919; Berthelot and Luginin, *Ann. chim. phys.*, [6] **13** (1888), 328.

Maleic: Landolt, p. 925; Luginin, *Ibid.*, [6] **1891**, 179.

This question of temperature control has been given considerable study in the past in connection with the oxidation of sulfur dioxide to sulfur trioxide, since too high a temperature results in the dissociation of the trioxide with a consequent loss in efficiency. In this case, however, the resulting dissociation products, SO_2 and O_2, may be recombined in a second catalytic zone at a lower temperature. In the case of maleic acid, when once burned it is safe to say that it cannot be regenerated from its combustion products.

The oxidation of ammonia to nitrogen oxides is a reaction which is more closely comparable to the oxidation of benzene in that without proper precautions undesirable reactions take place with a great heat evolution.

Calculation shows that the comparative exotherms per pound of starting substance are:

	B. t. u.
Benzene to maleic acid	± 10,560
SO_2 to SO_3	± 635.6
NH_3 to NO	± 5,660
Benzene to complete combustion	± 18,100
NH_3 to complete combustion	± 7,930

In these calculations the following figures have been used as heats of formation:

SO_2 + 69.26 kg. cal. per mol.	Berthelot, *Ann. chim. phys.*, [5] **22** (1881), 428; Landolt, p. 853.
SO_3 + 91.90 kg. cal. per mol.	Berthelot, *Thermo-chimie*, **2** (1897), 91; Landolt, p. 853.
H_2O + 58 kg. cal. per mol.	Berthelot and Matignon, *Ann. chim. phys.*, [6] **30** (1893), 553; Landolt, p. 850.
NO — 21.6 kg. cal. per mol.	Berthelot, *Ann. chim. phys.*, [5] **20** (1880), 260; Landolt, p. 854.
NH_3 + 12 kg. cal. per mol.	Berthelot, *Ann. chim. phys.*, [5] **20** (1880), 252; Landolt, p. 851.

The ammonia oxidation is assumed to proceed by the equation given by Landis.[1]

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O$$

If we are to consider temperature control for the production of maleic acid, nitric oxide and sulfur trioxide we must also calculate the amount of heat which can be carried away from the zone of reaction by the products.

We will assume that a 9 per cent ammonia-air mixture is used for the oxidation of ammonia (Landis), that the theoretical amount of oxygen as air is used for the oxidation of benzene to maleic acid and that in the oxidation of sulfur dioxide three molecules of oxygen are present for every two molecules of sulfur dioxide[1] and that the courses of the reactions are simple and not accompanied by side reactions. We will also assume that the reaction mixtures enter the converters at 25° C. and leave the catalytic zone at the temperature of the properly functioning catalyst which temperatures are assumed to be:

Ammonia oxidation	750° C. (Landis)
Benzene oxidation	400° C.
Sulfur dioxide oxidation	400° C. (Knietsch)

Without burdening you with our calculations, we arrive roughly at the following results:

REACTION	HEAT DEVELOPED	HEAT CAPACITY OF ENTERING GASES
$12N_2 + 2SO_2 + 3O \longrightarrow SO_3$	635	661
$32N_2 + 4NH_3 + 8O_2 \longrightarrow$ nitrogen oxides	5660	6264
$36N_2 + 2C_6H_6 + 9O_2 \longrightarrow C_4H_4O_4$	10560	1620

The calculations are based on the following values for specific heats:

MATERIAL	SPECIFIC HEAT	REFERENCE
SO_2	0.154	Regnault, *Mem. de l'Acad.*, **26** (1862), 1.
N_2	0.249	Schell and Heüse, *Tätigkeitsber. d. P.-T. Reichsanst. i. J.*, **1911**.
O_2	0.230	Holborn and Austin, *Sitzb. Akad. Wiss.*, Berlin, **1905**, 175.
NH_3	0.65	Nernst, *Z. Elektrochem.*, **16** (1910), 96.
C_6H_6	0.375	Regnault, *Mem. de l'Acad.*, **26** (1862), 1.

We inevitably found that even the refined apparatus developed for the control of these older reactions was unsuitable for such a "hair trigger" reaction as that of benzene to maleic acid.

Our laboratory apparatus for study of the reaction consists essentially of a combined vaporizer and mixer, a contact tube and condensing system. The vaporizer consists of a vessel containing benzene held at an exact temperature through which is passed a stream of air heated to the same temperature. The temperature of the vaporizer controls the benzene-air ratio used. The mixture then passes to a U-tube containing the catalyst immersed in a regulated metal bath. The products of reaction are passed through a series of absorbers—first water to remove maleic acid, then ice-cooled receivers to remove the bulk of the unreacted benzene, and finally oil scrubbers to remove the last traces of benzene. This is a mere skeleton outline of the set-up and we do not mean to burden you with a minute description of the meters, pressure and temperature regulators, special gas sampling devices, and numerous automatic condition recording devices, which make the apparatus when fully set up seem indeed formidable. Our experience, however, led us to add one device after another and the general set-up now in use for investigations is the result of two years' continuous development and application.

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[1] *Chem. & Met. Eng.*, **20** (1919), 473, 474.

[1] Knietsch-Lunge, 4th Ed., [3] 1, 1306.

With our laboratory contact tube a great mass of data has been collected in connection with the catalytic oxidation of such reactions as anthracene to anthraquinone, naphthalene to phthalic acid and naphthoquinone, benzene to maleic acid, and toluene to benzaldehyde and benzoic acid, in addition to similar reactions of numerous other hydrocarbons and their derivatives. It possesses the distinct advantage of a close approach to absolute temperature control which is so vital for the duplication of results under fixed conditions and the establishment of reliable data. It is, moreover, simple to manipulate, which is of importance in problems where a very large number of runs are necessary in order to accumulate a large mass of data before conclusions can be drawn safely. Advances are moreover being continually recorded toward improvement of design. Of course, a special vaporizer and a different form of condenser must be adopted for each raw material under investigation.

The reaction velocity of these partial oxidations appears to be without doubt much less than in the case of the oxidation of sulfur dioxide to sulfur trioxide and of ammonia to nitric oxide in the presence of platinum as a catalyst, and therefore the productive capacity of a converter of equal size is relatively small. This is an important factor in the design of large scale apparatus and coupled with the necessity for rapid heat removal to maintain a constant temperature, without being cumbrous and impracticable, makes the problem doubly difficult.

Definite progress has been made in our experimental manufacturing plant so that the problem of temperature control has been solved and large scale production now depends on the development of suitable tonnage uses for the products. We are able to furnish either maleic acid or its isomer, fumaric acid, in sample lots to those who may have an interest in their utilization. Many such possible uses are evident and are being thoroughly investigated. When you consider the very reactive nature of maleic acid, its anhydride and amide, the possibilities in pure chemical synthesis are unlimited. It opens up the possibility of the commercial production of many of the straight-chain acids such as fumaric, malic, succinic, aspartic, tartaric, propionic, lactic, acrylic, malonic, and hydracrylic acids. The use of these acids to replace those previously obtainable only from natural sources (mainly fruit juices) is receiving attention and has very decided possibilities.

In conclusion, we wish to express our sincere thanks to our Messrs. G. C. Bailey, F. A. Canon, A. E. Craver, L. A. Helfrich, W. J. Huff, J. F. W. Schulze, C. G. Stupp, and their some ten to a dozen assistants engaged on this problem, all of whom have contributed to the success of the undertaking and have by their earnest effort and teamwork made possible the development of the original discovery to a completed manufacturing process.

THE GENERATION OF HYDROGEN BY THE REACTION BETWEEN FERROSILICON AND A SOLUTION OF SODIUM HYDROXIDE[1]

By E. R. Weaver

Bureau of Standards, Department of Commerce, Washington, D. C.

Received May 16, 1919

DESCRIPTION OF THE FERROSILICON PROCESS

The generation of hydrogen by the reaction between ferrosilicon and a solution of sodium hydroxide is, in itself, an interesting process which has been extensively employed in recent years for filling military and naval balloons. The cost of materials makes the method expensive, but it has several great advantages, especially for use aboard ship and in portable units for field service. A very rapid rate of production of hydrogen can be secured from a comparatively small and inexpensive plant with very little labor and only sufficient power to operate the water pumps and stirring machinery. None of the materials used are combustible; they do not give off hydrogen until mixed, even when wet; and they are easily and safely transported and handled.

The principal reaction involved may be represented by the equation:

$$2\mathrm{NaOH} + \mathrm{Si} + \mathrm{H_2O} = \mathrm{Na_2SiO_3} + 2\mathrm{H_2} \qquad (1)$$

This equation probably represents the reaction taking place at the beginning of a run. However, sodium silicate in solution hydrolyzes, giving sodium hydroxide and hydrated silicic acid as indicated by the equation:

$$\mathrm{Na_2SiO_3} + (x + 1)\mathrm{H_2O} = 2\mathrm{NaOH} + \mathrm{SiO_2}.x\mathrm{H_2O} \qquad (2)$$

If we combine Equations 1 and 2, we have

$$\mathrm{Si} + (x + 2)\mathrm{H_2O} = \mathrm{SiO_2}.x\mathrm{H_2O} + 2\mathrm{H_2} \qquad (3)$$

While these equations may not represent all the complex compounds occurring in the solution, they probably represent the general course of the reaction, which thus appears to be in effect one between silicon and water, the sodium hydroxide serving as a catalyst. This viewpoint is important, since it shows that the relative amounts of alkali and ferrosilicon to be used in practice should be determined by the speed of reaction and the relative cost of the materials, rather than by computing the proportions corresponding to a definite equation.

The plant required for the production of hydrogen consists of three principal parts: (1) the solution tank in which the sodium hydroxide is dissolved, (2) the generator in which the reaction takes place, and (3) the washer, or condenser, in which the evolved gas is washed and cooled with water before being stored or put into the balloon. The generator controls should permit the operator to regulate the supply of sodium hydroxide solution, ferrosilicon, and water.

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[1] Published by permission of the Director of the Bureau of Standards. This work was done in connection with the use of the process for military purposes. It was shown that certain changes in the methods used by at least one of the allied nations would result in greatly facilitating generator operation with a saving of two-thirds of the sodium hydroxide and some of the ferrosilicon. The experiments, computations, and results, including specific operating directions for field generators, are given in considerable detail in the Fourth Annual Report of the National Advisory Committee for Aëronautics. This paper is intended only to present the method of investigation employed.

The operation of the generator is as follows: A predetermined charge of sodium hydroxide and water is stirred in the solution tank until solution is complete. A part or all of the solution is then run into the generator, and ferrosilicon added at such a rate as will best control the evolution of the gas. The heat of solution of sodium hydroxide is sufficient to start the reaction. The heat of this reaction increases the temperature rapidly, a large amount of water is evaporated, and it soon becomes necessary both to cool and dilute the mixture, by means of a cold-water spray within the generator. The process continues until the charge is exhausted.

RESULTS DESIRED

The results desired in the field, arranged approximately in the order of their military importance, are: (1) the production of hydrogen free from air and sodium hydroxide spray, and well cooled to prevent the condensation of water within the balloon, (2) maximum speed, (3) minimum weight of materials to be transported, and (4) minimum cost of materials. The relative importance of these requirements, and the best means of accomplishing the desired results will depend somewhat upon conditions. For example, when a balloon is to be sent up during battle, speed is usually of the utmost importance, but when the hydrogen is being placed in storage, purity and cost are the more important considerations.

A glance at these requirements shows that the rate of reaction and the total amount of hydrogen produced are the two most important elementary factors in the problem. Fortunately, these factors are easily studied on a small scale by permitting the reaction to take place under carefully controlled conditions and measuring with a gas meter, at frequent intervals, the amount of hydrogen produced. If the hydrogen yield is plotted against time, the rate of reaction at any time is represented by the slope of the curve at the corresponding point.

The reaction taking place in the generator occurs, of course, at the surface of contact of the ferrosilicon and the solution. If there is sufficient solution present to wet the solid completely, it is apparent that the rate of reaction is dependent only upon the amount of surface of the ferrosilicon, the composition of the two phases, and the temperature.

EXPERIMENTAL DATA

The experimental data required to establish the relation of these factors to rate of reaction are given in Figs. 1 to 9. The data were obtained in every case by the method outlined in the preceding paragraph. In general, only one curve is given for the variation in yield or rate of reaction produced by the variation of another condition because *the relative effect of changing one condition, the other conditions remaining constant, was found to be practically the same whatever values were chosen for the constant conditions.*

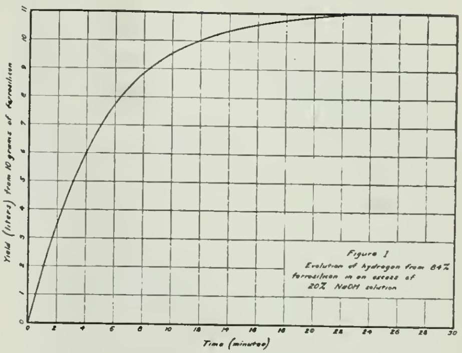


Figure 1
Evolution of hydrogen from 84% ferrosilicon in an excess of 20% NaOH solution

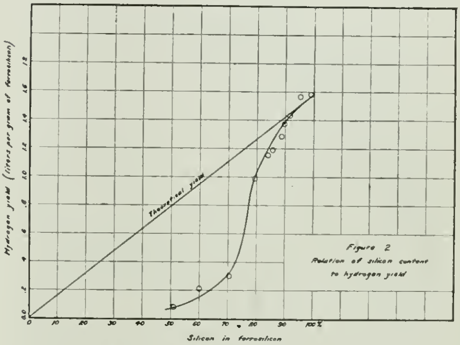


Figure 2
Relation of silicon content to hydrogen yield

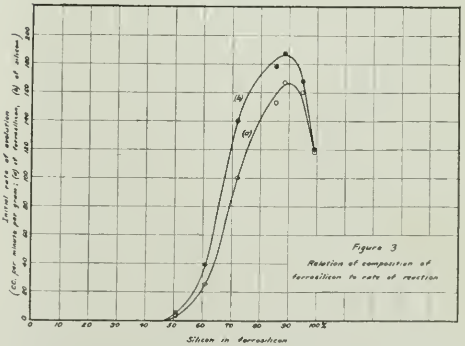


Figure 3
Relation of composition of ferrosilicon to rate of reaction

Fig. 1 represents the evolution of hydrogen from ferrosilicon (84 per cent silicon) in an excess of 20 per cent sodium hydroxide solution at a temperature of 100° C., and is typical of the data obtained by direct observation. By an excess of solution is meant an amount so large that the addition of a larger amount of solution was without appreciable effect on the results. The data represented by Figs. 2, 3, 6, 7, 8, and 9 were taken from more than one hundred curves of original observations similar to Fig. 1.

Fig. 2 shows the relation of silicon content to hydrogen yield under the conditions most favorable for obtaining a complete reaction. The very low yields obtainable from material containing less than 75 per cent of silicon are especially notable.

Fig. 3 shows the initial rate of evolution of hydrogen from ferrosilicons of different composition in 20 per

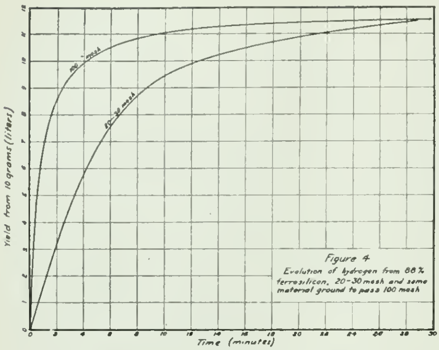


Figure 4
Evolution of hydrogen from 88% ferrosilicon, 20-30 mesh and same material ground to pass 100 mesh

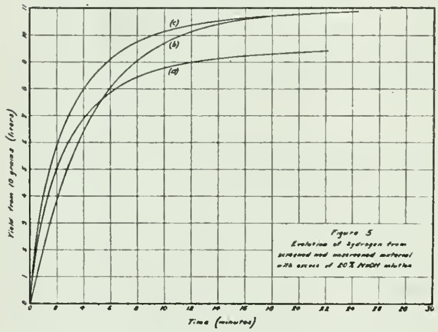


Figure 5
Evolution of hydrogen from screened and unscreened material with excess of 20% NaOH solution

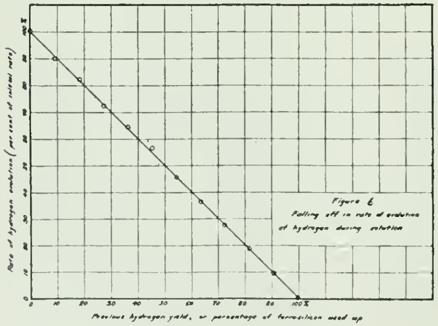


Figure 6
Falling off in rate of evolution of hydrogen during solution

cent sodium hydroxide solution at 100° C. The falling off in rate of reaction with increase in silicon content above 90 per cent may be due to the occurrence of more or less of the crystalline form instead of the amorphous form probably occurring in material of lower silicon content.

Fig. 4 represents the evolution of hydrogen from 88 per cent ferrosilicon crushed to pass a 20-mesh screen and retained by one having 30 meshes to the inch, and from material of the same composition crushed to pass completely a 100-mesh screen. The reaction took place in 20 per cent sodium hydroxide solution at 100° C.

A comparative test of material of a uniform size, and material containing large and small particles as it comes from the crusher was also desired. Such a comparison could not be made directly because a very great difference in composition exists between the coarse and fine material in commercial ferrosilicon, owing, no doubt, to the brittleness of the slag and other material low in silicon. An indirect comparison is shown in Fig. 5. Curve *a* shows the observed course of reaction of material crushed to pass a 16-mesh screen and having approximately the following proportions of the various sizes:

10 per cent failed to pass a 20-mesh screen
20 per cent passed a 20-mesh but failed to pass a 30-mesh screen
10 per cent passed a 30-mesh but failed to pass a 40-mesh screen
10 per cent passed a 40-mesh but failed to pass a 60-mesh screen
15 per cent passed a 60-mesh but failed to pass a 80-mesh screen
15 per cent passed a 80-mesh but failed to pass a 100-mesh screen
20 per cent passed a 100-mesh screen

Curve *b* shows the observed course of the reaction of the portion of the material which passed a 20-mesh and failed to pass a 30-mesh screen. It has already been shown by experiment (Fig. 4) that ferrosilicon of the same composition gives the same total yield of hydrogen whatever its fineness. Assuming the rate of reaction proportional to the percentage of silicon, the ordinates of Curve *c* were obtained by multiplying the ordinates of Curve *a* by the ratio of the total yield of hydrogen from 20- to 30-mesh ferrosilicon to the yield from the unscreened material. Curves *b* and *c* therefore represent the relative rates of the reaction of 20- to 30-mesh and unscreened material of the same silicon content.

Fig. 6 is a curve of unusual interest. The coördinates at any point represent the simultaneous values of the rate of evolution of hydrogen (expressed in percentage of the initial rate) and the amount of hydrogen previously evolved (expressed in percentage of the total yield obtainable from the material). These coördinates are used because they represent observed values; but it is obvious that the curve shows that the rate of reaction is at all times proportional to the amount of material unacted upon. This relation, which was totally unexpected, was verified again and again and was found to apply with equal accuracy to material retained by a 20-mesh screen, material which passed a 100-mesh screen, and mixtures of all sizes of particles. The result is of interest in connection with other processes since a similar relation will probably hold for the reaction of any irregularly crushed material surrounded by any fluid with which it reacts, provided the products do not accelerate or retard the reaction

The general statement has been made that the relative effect upon the rate of reaction of a given change in one condition is independent of the values of the conditions which do not change. The only exception noted was in the case of the relations between rate of reaction, concentration of solution, and amount of dissolved silicon. It was found that the relative effects of two given concentrations of sodium in the solution (regarded for the purpose of plotting results as sodium hydroxide, whatever the actual form of combination) upon the rate of reaction were very different in the presence of much or little dissolved silicon. In Fig. 7 the curve labeled "pure NaOH" represents the effect of dilution upon the initial rate of reaction when ferrosilicon is added to a fresh solution of sodium hydroxide. The curve labeled "2 g. Si : 3 g. NaOH" shows the approximate effect of dilution upon solutions containing 2 parts by weight of dissolved silicon to combined sodium equivalent to 3 parts of sodium hydroxide. The two curves in this figure are independent of each other and corresponding ordinates do not, of course, represent the same rate of reaction.

Fig. 8 shows the effect of dissolved silicon on the rate of evolution of hydrogen from a sodium hydroxide solution containing 20 per cent of the base at the beginning of the reaction. Since the amount of dissolved silicon could be determined only by measuring the gas evolved, the data are given in terms of hydrogen liberated.

Fig. 9 shows the effect of temperature upon the relative rates of reaction.

APPLICATION OF DATA TO CALCULATION OF GENERATOR CONDITIONS

The data required, in addition to the experimental results shown in Figs. 1 to 9, are available in published tables of physical and chemical constants. In order to apply the data it is necessary to assume a set of operating conditions such, for example, as the following, which will be called Generator Problem 1:

The generator is assumed to be an unprotected cylindrical tank 6 ft. 6 in. high, and 6 ft. in diameter, made of quarter-inch boiler plate; the solution tank, having about one-fourth the capacity of the generator, is assumed to have a heat capacity, including stirring machinery, equal to about half that of the generator. It is assumed that the air temperature is 20° C., the temperature of the water supply 18° C., the barometric pressure 740 mm. of mercury, and the wind velocity 10 miles per hour.

The charge is to consist of 363 kg. of ferrosilicon of the composition and fineness of the material represented by Curve *a* of Fig. 5.

Generation is to be started with a 30 per cent solution of sodium hydroxide made by dissolving 290 kg. of the alkali in 677 kg. of water. In order to heat the solution more quickly, only half the solution and 75 lbs. of ferrosilicon are introduced into the generator. When the temperature reaches 90° C. the ferrosilicon feed is started at the uniform rate of 15 lbs. per min. and continued until the charge has all been added. As soon as the ferrosilicon feed is started, the remainder of the solution is run into the generator at such a rate as to keep the temperature constant. When all the solution has been added, the constant temperature is maintained by the addition of cold water until the solution contains about 20 per cent of sodium hydroxide. The water is then stopped and no further effort made to control the reaction.

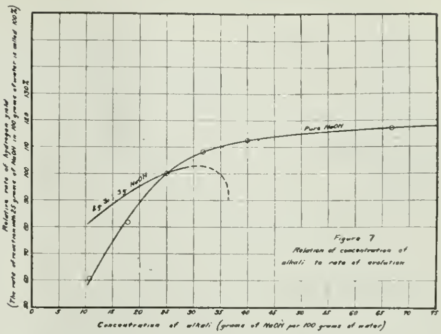


Figure 7
Relation of concentration of alkali to rate of evolution

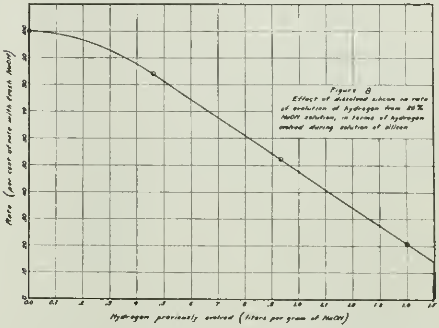


Figure 8
Effect of dissolved silicon on rate of evolution of hydrogen from 20% NaOH solution, in terms of hydrogen evolved during solution of silicon

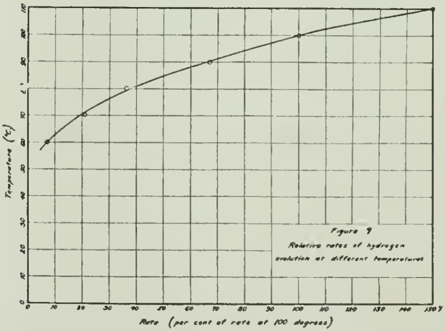


Figure 9
Relative rates of hydrogen evolution at different temperatures

From published data, the heat of solution of the sodium hydroxide in the water and the specific heats of the solution were obtained. From these and the assumed weight of the mixing tank and generator, the specific heat of iron, and engineering data concerning heat losses from radiators under given wind conditions, the initial temperature of the solution at the beginning of the reaction was determined. From the known composition and temperature of the solution, the weight of ferrosilicon in the generator, and the data of Figs. 5, 7, and 9, the initial rate of reaction was computed.

This rate was assumed to continue for one minute. From the amount of hydrogen evolved, the heat of reaction, the vapor pressure of the solution, the amount of water evaporated, the approximate heat losses from the surface to the generator, and the heat capacity of the generator and its contents, the temperature at the end of the first minute was computed.

In the same manner, similar data were computed for each minute up to the thirty-first and for each

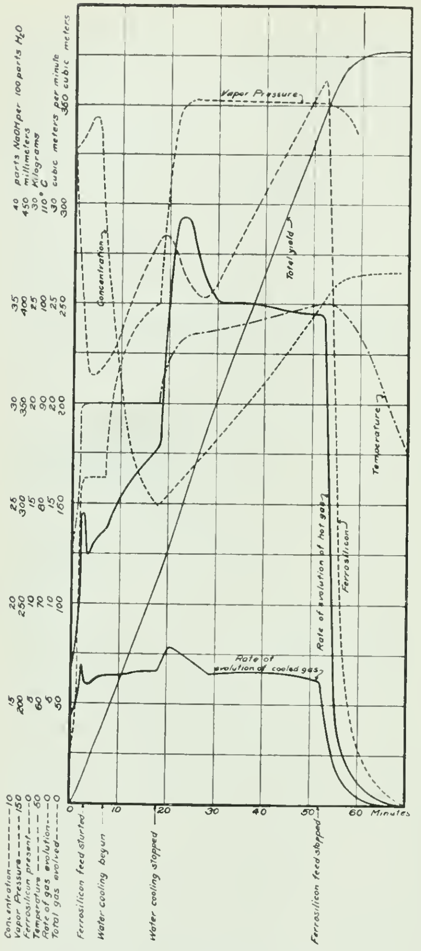


Fig. 10—Generator Problem 1

five-minute interval thereafter. In order to obtain a complete solution of the problem, it was necessary to determine, for each interval, the total hydrogen yield to the beginning of the interval, the temperature, the amounts of undissolved ferrosilicon, dissolved silicon, sodium hydroxide and of water present, the concentration of sodium hydroxide and dissolved silicon in the solution, the effect of each of these substances and of temperature upon the rate of reaction, the rate of reaction at the beginning of the interval, the vapor pressure of the solution, the water evaporated and the water added during the interval, the heat produced by the reaction, the heat lost by evaporation, radiation and convection, and the heat capacity of the generator and its contents.

Fig. 10 shows the values of the more important variables throughout the entire reaction under the conditions assumed. Starting with a relatively large amount of ferrosilicon and a small amount of solution in the generator, the temperature rises very rapidly to 90° C., the rate of evolution of gas increasing by more than 50 per cent. Fresh solution is introduced to keep the temperature constant, and the rate falls off as the ferrosilicon is used up. As soon as the ferrosilicon feed is started, the rate of evolution begins to pick up.

Conditions then remain practically static until all the solution is introduced and water has to be used for cooling. This immediately dilutes the solution, making the rate of reaction per gram of material progressively slower Ferrosilicon consequently accumulates gradually, the decrease in reaction from one cause almost exactly balancing the increase from the other. The more dilute solution has a greater vapor pressure and the total volume of hydrogen and steam leaving the generator increases considerably in consequence.

When the solution has been diluted to 20 per cent no more water is added. The temperature immediately begins to increase and the rate of reaction goes up, consuming ferrosilicon more rapidly than it is added. The temperature increase continues until the vapor pressure is so high that the heat of vaporization of the water evaporated, together with the heat loss from the surface of the generator, balances the heat of reaction. The excess of ferrosilicon is quickly used up and the rate of consumption of silicon once more drops to approximately the rate of addition. If the rate of reaction per gram of ferrosilicon were constant, the total rate of reaction would quickly become exactly equal to the rate of addition of ferrosilicon. There is, however, a continual change in the rate of reaction per gram caused by two factors: (1) the exhaustion of the sodium hydroxide, tending to decrease the rate, and (2) the gradual concentration of the solution as water is evaporated. Since the thermal equilibrium requires a nearly constant vapor pressure, the temperature must rise as the solution becomes more concentrated, and this factor tends to cause a considerable increase of rate of reaction per gram. The temperature increase is not quite sufficient to counterbalance the first effect and ferrosilicon again accumulates, while the rate of evolution falls off slightly. When the ferrosilicon is all added, it is quickly exhausted and the evolution of gas drops to a very low rate. Eight minutes after the addition of ferrosilicon stops, only 0.5 per cent of the 363 kilograms introduced into the generator remains unacted upon.

GENERATOR PROBLEM 2—Fig. 11 represents the rate of evolution (Curve *a*) and total yield (Curve *b*) from the same amount of ferrosilicon, with the same amount of sodium hydroxide and under the same weather conditions as were assumed in Problem 1, but with different conditions of operation. It is here assumed that enough water is added to the alkali in the mixing tank to make a 20 per cent solution, all of which is run into the generator at the start. The ferrosilicon feed is then started at the uniform rate of 15 lbs. per minute. No water is added during the run. Under these conditions nearly 15 min. are required to get the temperature up to a point at which the reaction goes on vigorously. By this time a large amount of ferrosilicon has accumulated and the rate of reaction becomes excessive.

Two additional curves representing the rate during the initial stage of generation under different methods of operation are shown. Curve *c* represents the result of operating under the same conditions as those represented by *a* except that only one-fourth of the solution is run into the generator at the start. Curve *d* represents the result of starting the run with 150 lbs. of ferrosilicon and one-quarter of the solution in the generator; no more ferrosilicon is added up to the point shown.

ACCURACY AND SIGNIFICANCE OF CALCULATED GENERATOR CONDITIONS

The computation of the quantities involved in such problems as those given is, of course, a laborious task; but it is much less so than might be supposed. After the computation is made for the first interval, few of the quantities require more than the reading of one point on a curve and a slide rule multiplication for their determination. Moreover a numerical error is usually easily detected, and even if undetected, it tends, in most cases, to eliminate itself in further calculation. If, for example, the computed temperature for one instant is too high, the computed rate of reaction and the vapor pressure of the solution will also be too high. The false rate of reaction will cause a decrease in the computed amount of ferrosilicon remaining which will automatically adjust the rate of reaction computed in the next few intervals to its correct value. The false vapor pressure will lead to the assumed evaporation of more water and the assumed addition of more cooling water which will dilute the solution and still further increase the vapor pressure and the cooling action due to evaporation while decreasing the rate of reaction. All these effects tend to decrease the temperature computed in the succeeding intervals until the correct temperature is again approximated. *Where the intervals chosen are short, only a systematic error running through a series of computations can have any serious effect on the result.*

In spite of this tendency for an error to become eliminated, the number of variables entering into such a computation is so great and the data used in some cases so unsatisfactory that any one numerical result cannot be regarded as possessing a high degree of accuracy. This is particularly true in the case of the calculations concerning the temperature changes in the generator. Thus in Problem 1 the time required to get the temperature of the generator up to 90° C. is computed to be about 3 min. It would not be at all surprising if the time required in practice were found to be 2 min. or 5 min. The data are hardly less useful on that account, however, since they enable one to compute, with a considerable degree of accuracy, the relative effects of the more important possible variations in generator operation, and indicate with certainty the direction and order of magnitude of almost any change in the conditions or methods of generation.

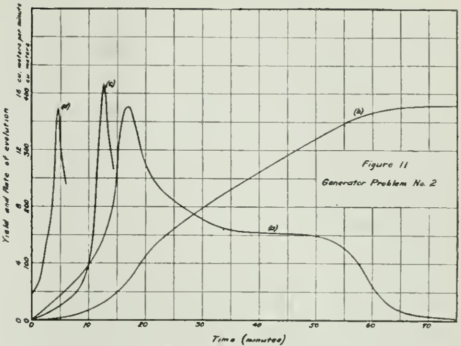


Figure 11
Generator Problem No. 2

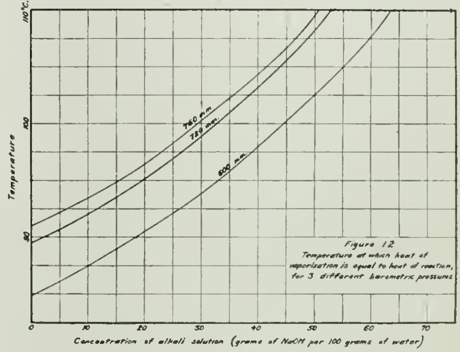


Figure 12
Temperature at which heat of vaporization is equal to heat of reaction, for 3 different barometric pressures

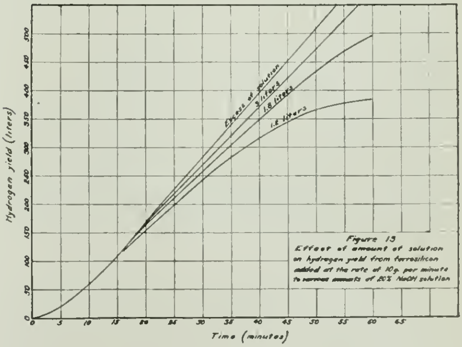


Figure 13
Effect of amount of solution on hydrogen yield from ferrosilicon added at the rate of 10g. per minute to various amounts of 20% NaOH solution

CONCLUSIONS FROM CALCULATED GENERATOR CONDITIONS

In spite of the many conditions affecting the rate of reaction of a given amount of ferrosilicon, the rate of evolution of gas over the major part of a generator run is primarily a function of the rate of addition of ferrosilicon. Whatever the conditions of temperature and concentration of solution, provided they are reasonably constant, and whatever the composition and fineness of ferrosilicon, if the ferrosilicon feed is regular, the material will accumulate in the generator until the amount of reacting surface is such that the rate of solution will closely approximate the rate of addition. Whether the rate of solution is greater or less than the rate of addition of material depends upon whether conditions are changing to make the rate of reaction per gram of ferrosilicon more or less rapid. The conditions must be so chosen that equilibrium will be quickly reached without generating gas at an excessive rate; that there will be no sudden variations of generator conditions, particularly of temperature, which will greatly disturb the established equilibrium; and that the material in the generator after the ferrosilicon is all added may be quickly and completely exhausted.

(1) TEMPERATURE CONTROL DURING GENERATION—The first requirement of successful operation is that the temperature of the generator be quickly raised at the beginning of the run to the point at which equilibrium is to be established, and that this be done without accumulating a large surplus of ferrosilicon in the generator. The ideal procedure is, of course, so to adjust conditions that when the temperature reaches the desired point, the amount of ferrosilicon in the generator will be just sufficient to produce hydrogen at the average rate for the run.

If the generator temperature is to be brought up only by the heat of solution of sodium hydroxide and the heat of reaction with ferrosilicon, it will be best to start with as concentrated a solution as can be quickly prepared and to use only a part of the solution with a comparatively large amount of ferrosilicon until the temperature reaches that at which it is desired to establish equilibrium. The ferrosilicon feed may then be started and more solution and water added as required to keep the temperature at the desired point.

The temperature chosen for equilibrium should be determined by the following considerations:

(*a*) It is desirable to have the rate of reaction per gram of ferrosilicon as rapid as possible at the end of the run in order to avoid waste of time and material.

(*b*) The rate of reaction per gram of ferrosilicon at the end of the run can be made a maximum, for a solution of given concentration, by permitting the temperature to rise until thermal equilibrium is established between the heat of reaction on the one hand and the heat of vaporization and other heat losses on the other.

(*c*) The rate of reaction per gram is increased by increasing the concentration of the solution, but the allowable change in this direction is strictly limited by the fact that concentrated solutions containing much dissolved silicon become very viscous. It is probable that, to utilize the materials economically, the solution at the end of the reaction should never contain more than 25 per cent of alkali calculated as sodium hydroxide.

(*d*) The temperature must be kept from changing rapidly at any time after approximate equilibrium is established. This is most readily accomplished by keeping it nearly uniform, and in order to fulfill the other requirements this working temperature must be slightly below the temperature at the end of the run.

Fig. 12 shows the temperatures at which the heat of vaporization of the water carried away from solutions of various concentrations will be equal to the heat of reaction. These are the maximum temperatures beyond which the generator temperature could not rise if there were no heat losses other than through evaporation. On a still, hot day, these temperatures will be approached closely if no cooling water is used. In very cold weather and especially when a strong wind is blowing, the maximum temperature obtainable will be several degrees lower.

The temperature of the generator should be allowed to rise at the beginning of the run to within 2° or 3° of the maximum temperature possible for the solution of the concentration desired at the end of the run. The temperature should be kept at this point by means of the water spray until the amount of water required is very small. The water should then be turned off entirely and the temperature allowed to rise gradually, as it will do. If this point is reached before the run is half over and the discharged sludge is very viscous, a lower operating temperature should be chosen for the next run. If water cooling is required up to the very end of the run. a higher operating temperature should be maintained.

(2) INITIAL CHARGE OF FERROSILICON—As already pointed out, the initial charge of ferrosilicon should be such that when the generator temperature reaches the desired equilibrium value, the rate of reaction will be the desired average rate for the run. In the case assumed in Problem 1 about 12 kg. of ferrosilicon containing about 70 per cent silicon were consumed in raising the temperature of the generator from 75° to 90° C. The temperature should have been raised to about 95° C. to avoid the irregularities in rate which resulted from too low a temperature.

The amount of silicon required to bring up the temperature of any desired quantity of solution can be obtained with sufficient accuracy from these data by simple proportion. The weight of ferrosilicon required to give any desired rate of gas production under the chosen conditions of temperature and concentration of solution is easily determined by experiment or computed from the data of Figs. 3, 5, 6, 7, and 9. The sum of the weights of ferrosilicon required for the two purposes is the amount which should be placed in the generator at the start.

(3) COMPOSITION AND FINENESS OF FERROSILICON—If the best conditions of temperature control and generator operation indicated above are adhered to, the relative advantage of using ferrosilicon having different rates of reaction on account of differences in composition or fineness is easily determined. If the temperature is fairly high it is only necessary to add, at the start, the amount of material determined in accordance with the principles discussed in the last section. The temperature will then quickly rise to the desired value, the time wasted with the more slowly reacting material being practically negligible. If the temperature is very low. however, it cannot be quickly raised with a slowly reacting material except by introducing so large an amount that the rate of reaction becomes excessive when the generator once gets hot. In some cases it might be impossible to produce sufficient reaction with low-grade material to balance surface heat losses; it would then be impossible to operate the generator at all. If, however aluminum is used, as it sometimes is, to start the reaction, there is little

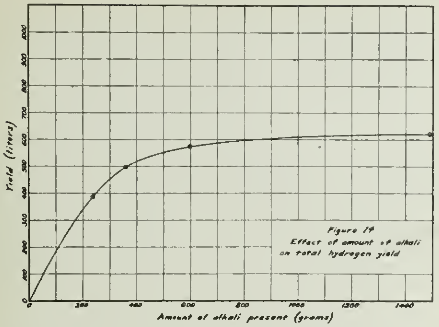


Figure 14
Effect of amount of alkali on total hydrogen yield

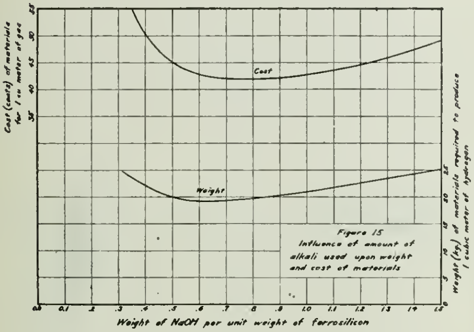


Figure 15
Influence of amount of alkali used upon weight and cost of materials

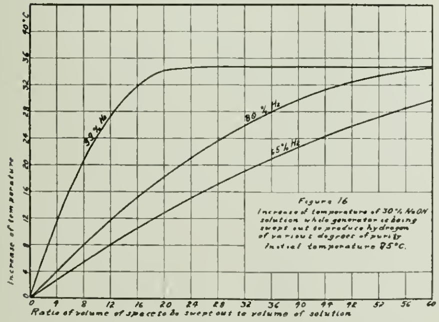


Figure 16
Increase of temperature of 30% NaOH solution while generator is being swept out to produce hydrogen of various degrees of purity
Initial temperature 75°C.

advantage so far as the initial stages of generation are concerned, in using a high-grade or finely powdered material.

When once the reaction is proceeding at the desired rate, and the temperature and rate of ferrosilicon feed are kept constant, it is obvious that generation will proceed at the same rate for both materials until all the ferrosilicon has been fed into the generator. The amount of ferrosilicon present is then inversely proportional to the rate of reaction per gram of material, and at whatever time the run is stopped the amount of material wasted in the two cases is in this same ratio. The amount wasted at the end of the reaction is not large if a reasonable time is allowed for the reaction to cease. The material assumed for Problem 1 was about as slow in acting as there will probably be occasion to use; the amount unattacked when the addition of material ceased was about 10 per cent; 5 min. later it was about 2 per cent; and in another 5 min. it had fallen to 0.5 per cent. It is clear, therefore, that even coarse, low grade material does not unduly prolong the period for reasonably complete reaction.

(4) AMOUNT OF SODIUM HYDROXIDE—Fig. 13 shows the total yield of hydrogen computed from the experimental data shown in Fig. 8 for the same amount of 88 per cent ferrosilicon added at the same constant rate to 4 different amounts of 20 per cent sodium hydroxide solution during a period of 1 hour, the temperature and concentration being assumed constant during the interval. The hydrogen yield during 60 min. under these conditions is plotted against amount of alkali in Fig. 14.

From the data of these curves were computed the total weight and the total cost of the ferrosilicon and sodium hydroxide (assumed to be 12.5 and 6 cents per lb., respectively) to produce 1 cm. of gas, assuming that the collection of gas ceases promptly at the end of the hour.

The results are given in Fig. 15, from which it appears that the greatest economy will be obtained by using about seven-tenths as much sodium hydroxide as ferrosilicon of this composition or about eight-tenths as much sodium hydroxide as silicon present in the material. There is, however, but little waste in using equal weights of ferrosilicon and sodium hydroxide, and such a practice would decrease the danger of obtaining very viscous solutions at the end of the run. On the other hand, it costs more to produce a given volume of hydrogen when too little sodium hydroxide is used only because ferrosilicon remains unacted upon at the end of the run. It has already been pointed out that the amount of material wasted decreases very rapidly when generation is permitted to proceed for a short time after the material is added; hence when haste is not an important object, greater economy could no doubt be secured by using a still smaller proportion of alkali.

(5) SWEEPING OUT THE GENERATOR—The first hydrogen coming from the generator is contaminated with the air in the generator at the beginning of the run, and should not be run into the balloon. If we make the assumption that the gases in the generator are at all times uniformly mixed, it can be shown that

$$R = \log_{e} \frac{1}{1 - \frac{a}{100}}$$

where R is the ratio of the volume of hydrogen evolved to the volume of the gas space in the generator, and a is the percentage of hydrogen in the space.

From this equation and the thermochemical data already given, it is possible to compute the rise of temperature of the generator and its contents under any given set of conditions before a gas of a given purity is obtained. Fig. 16 shows the increase of temperature, from an initial temperature of 75° C., corresponding to the production of hydrogen of 65, 80, and 99 per cent purity for all ratios of volume of gas space to volume of solution up to 60.

(6) OPERATING DIRECTIONS—The conclusions outlined above may be taken as representative of the information which is to be gained by the method of calculating the momentary variation of conditions during the process. Many minor conclusions have also been drawn which cannot be included in this paper for lack of space.

It was possible from these data to write a complete set of directions for the operation of a generator, and to indicate the means whereby the operator could determine when his methods were faulty. These directions have been made the basis of practice in the United States Navy and it may be said that such large scale tests as could be made without the installation of unjustifiably expensive machinery for quantitative measurement have failed to show that any of the conclusions drawn from the small scale experiments were at fault.

SUMMARY

The work done upon the determination of the best conditions for the operation of a hydrogen generator using ferrosilicon and a solution of sodium hydroxide is presented as an example of a somewhat unusual method of studying a complicated industrial process.

The author desires to express his indebtedness to Mr. W. M. Berry and Mr. V. L. Bohnson, who did most of the experimental work involved.

LOSSES INCURRED IN THE PREPARATION OF ACETONE BY THE DISTILLATION OF ACETATE OF LIME

By Leo Frank Goodwin and Edward Tyghe Sterne

Queen's University, Kingston, Ontario

Received September 9, 1919

In the commercial production of acetone by the destructive distillation of calcium acetate, the quantity of crude acetone obtained is very far from that to be expected from the analysis of the acetate. Guttmann[1] states that the acetone yield is only about 75 per cent of the theoretical, *e. g.*, 100 kg. of 80 to 82 per cent calcium acetate should yield theoretically about 30 kg. of acetone, but in practice only about 22.5 kg. of crude acetone are obtained, and on purification this is still further reduced to 20 to 21 kg. acetone of British War Office specification acetone. Yields as high as 25 kg. of raw acetone per 100 kg. acetate of lime are claimed by some manufacturers, but the general average at the time this investigation was started appeared to be 22 to 23 kg., a yield of only 75 per cent of the theoretical.

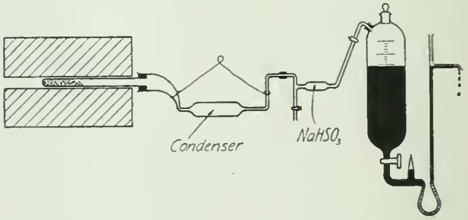
When discussing the subject with manufacturers it was usually stated that the amount of gases evolved through decomposition was small, but that they carried off an inappreciable amount of acetone, which it did not pay to recover. It became of interest therefore to study this low yield—if not simply due to defects in manufacture—to see how much was lost by decomposition of the acetone through contact with the walls of the heating tubes, and to determine the amount of gases evolved as well as the acetone entrained by them.

This investigation was started in 1913 and completed in April 1914. Absence of the senior author at the war made earlier publication impossible.

To attain the object of the investigation it was necessary to employ as small an amount of acetate as possible in order to ensure uniform and rapid heating. Since no difficulty is involved in condensing and accurately weighing the products formed and measuring the gases evolved, amounts of 5 or 10 g. should yield accurate results. The ratio of the surface of the heated tube, compared to the acetate used, was much larger than that obtaining in practice.

DESCRIPTION OF APPARATUS

The apparatus used, as shown in the figure, consisted of a decomposition tube for heating the calcium acetate, a suitable condenser for the collection of the crude acetone, a trap for the retention of the acetone contained in the gases, and a gas holder for collecting them.



The decomposition tube consisted of a piece of Jena glass tubing of about 16 mm. bore, and 14 in. long, sealed at one end, and heated in a horizontal electric tube furnace wound with nichrome ribbon. The furnace was calibrated by means of a platinum-platinum rhodium thermocouple, and the heating current plotted against the temperature. A constant heating zone of 3 in. was obtained in the middle of the furnace.

The capacity of the condenser employed must be as small as possible compared with the volume of the gases produced. The condenser consisted of a 25 cc. pipette bent as shown in the figure with an adapter fused on to one end. This adapter fitted over a piece of rubber tubing, slipped over the end of the decomposition tube, and made an air-tight joint, exposing a minimum of surface for the absorption of acetone vapors by the rubber.

Inasmuch as the amount of acetone carried away by the decomposition gases was to be determined, the condenser was cooled in ice and water only, so as to imitate conditions obtaining in practice, where cold water only is used.

The acetone trap consisted of a 5 cc. pipette bent similarly to the condenser. A side tube was fused on near one end to enable the apparatus to be filled initially with nitrogen and to draw off gas samples at the end of a run. The most satisfactory gas-collecting device was found to be that shown in the figure. A cylindrical graduated separating funnel of one liter capacity was fitted with an overflow tube to allow the mercury in this gas holder to flow out as the gases were collected. The level of this overflow tube was adjustable so that the gases could be kept at atmospheric pressure. An air trap was sealed to the bottom of the gas holder.

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[1] "The Manufacture of Explosives," Vol. I.

EXPERIMENTAL DETAILS

Experiments were first made with pure anhydrous calcium acetate (99.2 per cent, 2 g. distilled with phosphoric acid required 25.18 cc. *N*/10 NaOH). The gray crude acetate subsequently used was anhydrous and 81.8 per cent pure (2 g. required 20.70 cc. *N*/10 NaOH).

In Expts. 1 to 12, 10 g. of the acetate were used for decomposition, but only 5 g. were used in subsequent experiments to ensure more uniform heating.

In Expts. 1 to 13 the acetate was placed in the decomposition tube, the condenser packed in ice and when the whole apparatus had been made tight, the experiment was started. The amounts of acetone and water produced were found by weighing the condenser, and the gases in the gas holder were analyzed.

In Expts. 15 to 21, the apparatus was assembled ready for an experiment, the acetate placed in the decomposition tube and the trap charged with 2 cc. of sodium bisulfite solution (25 per cent) to retain traces of acetone. The side tube of the trap was then connected to a glass Y-tube, one arm of which was connected to a cylinder containing compressed nitrogen, and the other to a vacuum pump and manometer. The glass tap connecting the gas holder with the rest of the apparatus was then closed. The apparatus was then exhausted to about 30 mm. of mercury and nitrogen admitted from the cylinder. This was repeated four or five times, and the rubber tubing on the side tube then closed by a screw pinchcock and glass rod. The gas-holder tap was then opened and after the whole apparatus had been proved air-tight by lowering the discharge tube of the gas holder the heating current was turned on. In Expts. 1 to 19, the gas holder contained water, and in Expts. 20 and 21 mercury.

The experiments were run for 3 or 4 hrs. at a temperature of 620° C. In Runs 15 to 21 the temperature was finally raised to 880° C. for one hour to ensure complete decomposition.

The actual amount of acetone and its homologs in the condensate was not determined, since the composition of this condensate is well known.

The acetone caught by the bisulfite solution was estimated by Messinger's method as follows: The washings from the trap were made alkaline with NaOH and distilled until three-fourths had been condensed in a small wide-mouthed flask. 25 cc. of normal NaOH were added and the mixture allowed to stand 5 min. *N*/10 iodine solution was then run in little by little until the upper portion became clear on standing for one minute, and 25 per cent excess was then added. After standing for 20 min., a slight excess of normal H_2SO_4 was added and the liberated iodine titrated with standard sodium thiosulfate solution, using starch solution as indicator. 1 cc. *N*/10 iodine solution = 0.96 mg. acetone.

At the end of the experiment the tap leading from the bisulfite trap to the gas holder was closed. A sample of the gases left in the apparatus was then withdrawn through the side tube in the trap into a gas burette filled with mercury. By noting the pressure in the burette and reducing the volume of gas thus withdrawn to normal temperature and pressure, it is possible to calculate the volume of the decomposition and trap part of the apparatus as follows:

$$V = V_1 \frac{(P-d)}{d}$$

Where V = volume of apparatus
V_1 = volume of gas drawn off under atmospheric pressure P
P = atmospheric pressure
d = difference in height of mercury columns in burette and levelling tube

Samples of the gases in the gas holder and of the gas drawn off at the end of the run were analyzed for carbon dioxide, oxygen, carbon monoxide, and ethylene in the usual way. To part of the residue from the ethylene determination an approximately equal volume of oxygen was added and hydrogen estimated by combustion over palladium asbestos. Methane was then determined in the residue by explosion. An Orsat-Lunge apparatus was used.

The following are the data for a typical experiment:

RUN 13

Charge = 5 g. pure calcium acetate (99.2 per cent), giving theoretically 1.835 g. acetone.

Started 2 P.M., current 2 amps. = 620° C.
Stopped 7.30 P.M., current 2 amps.
} Total time $5^1/_2$ hrs.

Gas collected in gas holder 100 cc. first 2 hrs., total of 340 cc.

Acetone and water condensed = 40.50 — 38.77 = 1.73 g.

Acetone collected in trap required a net amount of 27.12 cc. iodine solution (*N*/10) = 26 mg. acetone.

Total acetone = 1.756 g. = 96.2 per cent yield.

The combined results of experiments with pure and with crude calcium acetate are given in Table I.

TABLE I—YIELD OF ACETONE

RUN No.	Quality	Time Hrs.	Max. Temp. ° C.	Vol. of Gas Evolved Cc.	Acetate Used G.	Theoretical Yield of Acetone G.	Acetone in Condenser G.	Acetone in Trap G.	Yield Per cent
11	Pure	4.5	620	500	10	3.67	3.55	0.025[1]	97.4
12	Pure	4	620	750	10	3.67	3.42	0.025[1]	93.8
13	Pure	5.5	620	340	5	1.83	1.73	0.026	96.2
15	Pure	5.75	880	325	5	1.83	1.79	0.025	99.0
18	Pure	4.5	880	500	5	1.83	1.73	0.026	96.0
20	Pure	4.5	880	225	5	1.83	1.72	0.024	95.3
								AVERAGE	96.3
8[2]	Crude	4	620	350	10	3.009	2.52	0.090	86.8
9[2]	Crude	4	620	600	10	3.009	2.94	0.020	98.3
16	Crude	5	880	540	5	1.504	1.44	0.013	96.5
17	Crude	5	880	680	5	1.504	1.28	0.070	89.8
19	Crude	5	880	670	5	1.504	1.48	0.030	98.5
								AVERAGE	94.0

[1] Estimated.

[2] In Expts. 8 and 9 a less suitable condenser of 125 cc. capacity had been used

From these figures it is evident that the volume of gas evolved is roughly proportional to the amount of acetate decomposed, and little influenced by the final temperature in the tube. The final heating for 1/2 to 1 hr. at 880° can naturally only decompose traces of acetone still left in the tube.

The average yield of raw acetone and water is 96.3 per cent for pure acetate, against 94.0 for crude, the amount of gases formed through decomposition being approximately twice as much for the crude acetate as for the pure.

Table II shows the amount of acetone carried off by the decomposition gases in the various experiments and also the degree to which the gases were saturated with acetone vapor.

Table II—Acetone in Decomposition Gases

Run No.	Acetone in Trap Mg.	Per cent of Total Recovered in Bisulfite Solution	Vol. of Gases Produced Cc.	Mg. of Acetone when Saturated	Saturation of Gas Per cent	Acetate Used
13	26	1.5	340	73	36	Pure
15	25	1.4	325	70	36	Pure
16	13	0.86	540	116	11	Crude
17	69	5.1	680	146	47	Crude
18	26	1.5	500	107	24	Pure
19	34	2.3	670	144	24	Crude
20	24	1.4	225	43	56	Pure
	Average	2.0		Average	33	

The percentage saturation of the gases with acetone was calculated from the vapor pressure of acetone at 0° C. This value, calculated by applying Ramsay and Young's formula to similar liquids whose vapor pressure is known down to 0°, was found to be 63 mm. of mercury.

1 cc. acetone vapor at 0°, 760 mm. weighs 2.589 mg.
100 cc. gas can carry at 0° C. and 760 mm. pressure

$$2.589 \times 100 \times \frac{63}{760} = 21.47 \text{ mg. of acetone}$$

It is therefore concluded that under conditions simulating practice, the average saturation of the gases is 33 per cent, and that about 2 per cent of the acetone is lost with the gases formed during distillation, and can be recovered by means of absorption in sodium bisulfite solution. This has been done for many years in the case of the vapors issuing from cordite drying stoves, and in celluloid manufacture, and could well be applied to acetone manufacture.

A sample calculation to a nitrogen-oxygen-free basis is given below.

Run 15

Volume of gas in holder 325 cc., 5.8 per cent CO_2, 1.8 per cent O_2, 16.0 per cent CO, 12.4 per cent H_2, 10.7 per cent CH_4, 53.3 per cent N_2.

Volume of residual gas in apparatus 157 cc., 0.4 per cent CO_2, 0 per cent O_2, 42.6 per cent CO, 5.1 per cent H_2, 33.5 per cent CH_4, 12.7 per cent C_2H_4, 5.7 per cent N_2.

	Cc. in 325 Cc. Holder Gas	Cc. in 157 Cc. Residual Gas	Total Cc.	Per cent Reckoned on Pure Gases
CO_2	18.8	0.6	19.4	6.5
CO	52	68	120	40.5
C_2H_4	...	20.3	20.3	6.9
CH_4	34.8	53.5	88.3	29.6
H_2	40	8.2	48.2	16.3
O_2	5.8	..	(5.8)	..
N_2	173	9.1	(182.1)	..
			Total	99.8

Nitrogen found = 173 + 9.1 = 182.1 cc.
Nitrogen calculated = 157 + 5.8 × 4 = 180 cc.

Assuming a condenser temperature in practice of 10°, 33 per cent saturation, and a vapor pressure for acetone of 115 mm. at 10°, the amount of acetone carried away by the decomposition gases amounts to 0.8 kg. per 100 kg. of acetate distilled, a not inconsiderable loss.

In Table III the composition of the gases evolved has been calculated to an oxygen-nitrogen-free basis. In nearly all cases the total volume of nitrogen agreed closely with the sum of the volume originally present in the apparatus and that due to leakage, as calculated from the amount of oxygen present by multiplying by 79/21. In one or two experiments no oxygen was found, but an excess of nitrogen, and in these cases the oxygen seems to have been used up by the preferential combustion of some of the gases evolved, chiefly the methane.

The average composition of the gases evolved compares fairly well with that found by Barbier and Roux[1] on passing the vapor of acetone through a red-hot copper tube.

Table III—Composition of Gases

Run No.	Quality	Acetate Used G.	Net Vol. Gas Evolved Cc.	CO_2 Per cent	CO Per cent	H_2 Per cent	CH_4 Per cent	C_2H_4 Per cent
15	Pure	5	296	6.5	40.5	16.3	29.6	6.9
18	Pure	5	409	10.4	50.4	20.4	17.2	1.8
20	Pure	5	142	9.9	35.1	17.7[1]	34.3[1]	4.1
21	Pure	5	176	8.4	38.5	27.6	21.7	4.0
		Average	265	8.8	41.1	20.5	25.7	4.2
16	Crude	5	540	11.2	57.8	25.0	2.2	3.8
17	Crude	5	622	17.0	61.0	16.4	5.1	0.2
19	Crude	5	549	19.3	62.5	17.1	0.5	0.5
		Average	577	15.8	60.4	19.5	2.6	1.5
Barbier and Roux			...	..	39.2	17.5	37.5	5.6

[1] Estimated.

Some tarry products were formed even with pure acetate, but no attempt was made to determine their amount or composition. With crude calcium acetate the amount of tar was considerably greater and a much larger average volume of gas was evolved.

The composition of the gases formed from the crude acetate differs considerably from those evolved on decomposing the pure acetate, but this is probably due to the organic impurities in the crude salt. CO_2 and CO are present in larger quantities, while the percentage of methane and ethylene is much reduced.

CONCLUSIONS

As was to be expected, the decomposition of calcium acetate by heat into acetone and calcium carbonate is almost quantitative, any gases formed arising through the decomposition of acetone in contact with the heated walls of the containers, or in the case of commercial calcium acetate through decomposition caused by the tarry impurities.

The poor yields obtained in practice are therefore due to defective apparatus, and it is known that since this investigation was completed, considerably higher yields are being obtained. It should still be considered whether it would not be worth while to recover the acetone vapors carried away by the decomposition gases, since they may possibly carry away 0.8 kg. of acetone out of a total yield of 22 to 24 kg.

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[1] *Compt. rend.*, **102**, 1859.

SUMMARY

1—An investigation was undertaken to elucidate the low yield obtained in practice in the manufacture of acetone by the distillation of gray acetate of lime. An apparatus of small volume was designed to be reasonably air-tight, and the distillation carried out in an atmosphere of nitrogen.

2—The gases formed were measured and analyzed, and reduced to a nitrogen-oxygen-free basis. Their composition was approximately the same as the gases formed by passing acetone through heated tubes.

3—The yield of acetone was determined, and the amount of acetone carried away by the decomposition gases ascertained.

4—The decomposition of calcium acetate, as was to be expected, was found to be nearly quantitative, any losses in practice being therefore due to defective apparatus.

THE FORMATION OF THE DOUBLE SALTS OF CALCIUM AND POTASSIUM SULFATES AT 100° C.

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Received September 30, 1919

In a recent paper[1] on "The Double Salts of Calcium and Potassium and Their Occurrence in Leaching of Cement Mill Flue Dust," some of the hitherto published data on the conditions necessary for the formation and stability of these double salts were discussed. It was also stated that since there had apparently been no equilibrium determinations made for the commercially important temperature of 100° C., some tests were being made at the laboratories of this company to determine, if possible, the equilibrium concentration of potassium sulfate, for the formation both of syngenite and potassium penta-calcium sulfate. In the present paper the results of these tests are described.

The object was to determine the equilibrium concentration of K_2SO_4 in solution at 100° C. for the two equations:

$$5(CaSO_4.2H_2O) + K_2SO_4 \rightleftarrows K_2SO_4.5CaSO_4.H_2O + 9H_2O \quad (1)$$

$$K_2SO_4.5CaSO_4.H_2O + 4K_2SO_4 + 4H_2O \rightleftarrows 5(K_2SO_4.CaSO_4.H_2O) \quad (2)$$

METHOD

The method used was similar to the one employed by Cameron and Brezeale[2] for experiments at lower temperatures.

In the first part of the present tests, known weights of water, K_2SO_4, and $CaSO_4.2H_2O$ were agitated in stoppered bottles in a bath of boiling water for several days, and the final solution rapidly sampled and analyzed for K_2O, CaO, and SO_3. In the last part previously prepared syngenite and potassium pentacalcium sulfate were used in place of the gypsum.

The flasks were of the ordinary round-bottom form of 250 cc. capacity, and were rotated in the water bath in the manner usually employed for thermostatic work. As only 150 cc. of water were used in each flask, good agitation was obtained.

The temperature of the water was that of slowly boiling tapwater at the altitude of Los Angeles (about 250 ft. above sea level). Any error introduced by assuming this temperature to be 100° C. is slight compared with the ordinary errors of the chemical analysis of the solution.

The time of agitation varied from 7 to 23 days. It is probable, however, that the reactions had gone to completion or reached equilibrium in less than 7 days in each case.

In starting a run, 150 cc. of distilled water, together with the determined weight of "Baker's Analyzed" potassium sulfate and calcium sulfate, were put in the flask. The flasks were then carefully heated over the Bunsen burner until the air in the water and space above had been driven out, then closed with rubber stoppers, placed in the agitation frame in the water bath, and agitated continuously until the end of the run.

At the completion of the run the solutions were quickly withdrawn from the flasks, filtered, and later analyzed. In certain tests the solids were also washed and their composition determined. In some cases the potash only was determined by the cobaltinitrite method, and the potassium sulfate content calculated from this determination, while some solutions were also analyzed for lime and sulfates, and the potassium sulfate content calculated by difference.

In making the tests for the determination of the equilibrium concentration of potassium sulfate for the formation of potassium penta-calcium sulfate according to Equation 1, the amounts of potassium sulfate and gypsum added were such that the initial potassium sulfate concentration would be well above the probable equilibrium point, while the final concentration that would result if all of the gypsum added were converted to the penta-salt would be less than this equilibrium concentration. The probable equilibrium concentration was found by extrapolation from D'Ans' diagrams given in the previous paper.[1]

If the proportion of potassium sulfate and gypsum were correctly chosen part of the gypsum would combine with potassium sulfate to form potassium penta-calcium sulfate, thereby lowering the potassium sulfate concentration to the equilibrium point. The final products would then be a mixture of gypsum and potassium penta-calcium sulfate in equilibrium with the potassium sulfate solution. If, on the other hand, the initial potassium sulfate concentration were equal to or less than the equilibrium concentration no combination would take place and the final solution would be the same as the initial one; while if the initial concentration were so high that all the gypsum could combine as the penta-salt without lowering the concentration to the equilibrium point, the difference between the initial and final concentration of potassium sulfate would correspond to the amount of potassium penta-calcium sulfate formed from all the gypsum added.

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[1] This Journal, 11 (1919), 327.

[2] *J. Phys. Chem.*, 8 (1904).

[1] *Loc. cit.*

The equilibrium concentration thus determined was then checked by starting with a potassium sulfate solution slightly below the equilibrium point and adding previously prepared potassium penta-calcium sulfate. Part of the penta-salt would then break up to form gypsum, thereby increasing the potassium sulfate concentration in solution to the equilibrium point.

By similar means the equilibrium concentration for the formation of syngenite in accordance with Equation 2 was determined. Here the relations are of course slightly more complicated, since all the gypsum added must in all cases combine either as syngenite or as the penta-salt. Here the first results were checked by adding previously prepared syngenite to a potassium sulfate solution below the equilibrium point, and by adding potassium penta-calcium sulfate to a potassium sulfate solution above that point, thus approaching the equilibrium from both sides.

Two sets of tests were also made where the proportions of the constituents were such as to lead, in one case, to the formation of syngenite only, and in the other case to the formation of potassium penta-calcium sulfate only. In these tests the solid phases were separated and analyzed.

The syngenite was prepared by combining 120 g. of potassium sulfate in 1000 cc. of water with 20 g. of calcium chloride in 100 g. of water. The mixture was allowed to stand several weeks at room temperature with frequent agitation, after which the precipitate was filtered, rapidly washed with cold water, and dried at 110° C.

The salt had the composition shown in Column A. Column B gives the theoretical composition.

	A	B
K_2O	28.74	28.70
CaO	16.95	17.06
SO_3	48.90	48.73
Loss on ignition	5.65	H_2O 5.49

The potassium penta-calcium sulfate was prepared by mixing 500 cc. of a 15 per cent potassium sulfate solution with a solution of 38 g. of calcium chloride in 100 cc. of water. The mixture was boiled several hours, and the precipitate separated, treated with 200 cc. of 10 per cent potassium sulfate solution, and boiled for one hour. The precipitate was filtered off, washed rapidly with cold water, and dried at 110° C.

This salt had the composition shown in Column A, while Column B gives the theoretical composition:

	A	B
K_2O	11.24	10.80
CaO	31.47	32.10
SO_3	55.40	55.00
Loss on ignition	2.30	H_2O 2.10

THE POTASSIUM PENTA-CALCIUM SULFATE–GYPSUM EQUILIBRIUM

Table I gives data and results from the test for the potassium penta-calcium sulfate-gypsum equilibrium.

In Table I the figures of the column headed "Initial Composition" are calculated from the amounts of potassium sulfate, etc., added to the given amounts of water. The values headed "Final Composition" are those obtained from analysis of the final solution. In the case of the K_2SO_4, those headed "From K_2O" were calculated from the cobaltinitrite potash determination, while those headed "From CaO + SO_3" were calculated from the lime and sulfate determinations on the basis that all the SO_3 was present in the solutions either as $CaSO_4$ or K_2SO_4.

TABLE I

		INITIAL COMPOSITION BY CALCULATION G. per 100 G. H_2O Solids and Solutions			FINAL COMPOSITION G. per 100 G. H_2O					
					Of Solution by Analysis				Of Solids by Calculation	
					K_2SO_4					
No.	Days	K_2SO_4	$CaSO_4$	Penta-Salt	From K_2O	From CaO $+SO_3$	Av.	$CaSO_4$	$CaSO_4$	Penta-Calcium Sulfate
1	7	0.90	1.33	0	0.91	..	0.91	...	1.14	0
2	7	0.90	1.33	0	0.89	..	0.89	...	1.14	0
3	9	1.20	3.33	0	..	1.19	1.19	0.192	3.14	0
4	23	1.50	3.33	0	0.95	..	0.95	...	0.99	2.76
5	9	1.50	3.33	0	1.19	1.23	1.21	0.155	2.07	1.45
6	8	1.50	3.33	0	1.14	..	1.14	...	1.41	1.80
7	10	0.80	0	2.50	1.02	0.86	0.94	0.202	0.35	1.80
8	10	0.80	0	2.50	0.92	0.84	0.88	0.182	0.13	2.10

The final composition of the solids in the last two columns had been calculated from the other data, using the average of the K_2SO_4 analysis in each case. These figures show that two solid phases were present only in the last five tests, so equilibrium could not have been reached in any of the others.

Two factors must be borne in mind when considering the results given above. One of these is the possibility of analytical errors, which are particularly liable to occur in the analysis of potash. The other is the possibility that the added gypsum may become so coated with the double salt that correct equilibrium conditions cannot be reached. This latter tendency was particularly noticeable, due probably to the high initial reaction velocity at the temperature used, and even though the agitation of the flasks was kept as rapid as seemed safe, the lumps formed from the gypsum in the beginning of the tests did not always break up.

Considering the figures given for the final potassium sulfate concentration in the first three tests, it appears that the equilibrium concentration lies above 1.19 g. of K_2SO_4 per 100 g. of H_2O, since no double salt appeared to have been formed in any of these tests. In Tests 4 to 6, where part of the gypsum added was changed to the double salt, the final concentration varies from 0.95 to 1.19 g. K_2SO_4 per 100 g. H_2O. In Tests 7 and 8 the equilibrium was reached from a lower concentration. The figures for the final potassium sulfate concentration in these tests are not very satisfactory as far as agreement of analyses is concerned, but this concentration appears to lie between 0.84 and 1.02 g. K_2SO_4 per 100 g. of H_2O.

For want of more accurate data a fairly close approximation of the potassium sulfate concentration at equilibrium can probably be reached by taking the mean of all the determinations made in Tests 4 to 8, where the conditions were such that equilibrium should have been reached.

This average is

1.02 g. K_2SO_4 per 100 g. of water

or

1.00 g. K_2SO_4 per 100 g. of solution.

The mean $CaSO_4$ concentration in Tests 6 to 8 was

0.180 g. per 100 g. of H_2O.

Calculating these results to moles per 1000 moles of H_2O gives

For K_2SO_4 = 1.05
For $CaSO_4$ = 0.24.

The values given by D'Ans for the K_2SO_4 concentration were 3.8 moles at 40° C., 2.4 moles at 60° C., and 1.3 moles at 83° C.

THE SYNGENITE—POTASSIUM PENTA-CALCIUM SULFATE EQUILIBRIUM

In making tests for the determination of the equilibrium of the equilibrium concentration for the syngenite—potassium penta-calcium sulfate equilibrium according to Equation 2, the most likely value deducible from the previous determinations[1] appeared to be about 12 moles of K_2SO_4 per 1000 moles of H_2O.

This proved to be too high. A number of tests were therefore made which resulted only in the formation of approximately the theoretical amount of syngenite from the gypsum added. Only those tests will therefore be reported where the final conditions were at or near those required for the equilibrium.

The data and results from these tests are given in Table II, where the various readings have similar significance to those in Table I.

TABLE II

		Initial Composition G. per 100 G. H_2O Solids and Solution				Final Composition G. per 100 G. H_2O Of Solution by Analysis K_2SO_4			Of Solids by Calculation	
No.	Days	K_2SO_4	$CaSO_4$	Syngenite	Penta-Salt	From K_2O	From CaO + SO_3	$CaSO_4$	Syngenite	Penta-Salt
1	9	10.00	10.00	0	0	7.18	6.83	0.139	0	12.65
2	9	10.00	10.00	0	0	7.10	7.15	0.100	0	12.70
3	9	11.50	3.33	0	0	9.90	10.07	0.097	1.59	3.30
4	9	13.00	3.33	0	0	8.58	8.86	0.115	7.80	0
5	8	13.00	3.33	0	0	9.79	...	...	5.60	1.17
6	8	13.00	3.33	0	0	9.88	...	...	5.38	1.28
7	9	16.00	3.33	0	0	11.15	10.51	0.085	7.84	0
8	9	16.00	3.33	0	0	11.35	10.70	0.085	7.84	0
9	10	8.00	0	3.77	0	8.90	8.76	0.108	1.87	0.87
10	10	8.00	0	3.77	0	8.90	8.74	0.108	1.87	0.87
11	10	10.00	0	0	5.84	9.06	9.21	0.102	4.58	2.12
12	10	10.00	0	0	5.84	9.10	8.91	0.112	4.41	2.43

The composition of the solids in all tests except 1, 2, 7, and 8, has been calculated from the difference between the average initial and final potassium sulfate concentration and the available calcium sulfate. In Tests 1 and 2, however, all the calcium sulfate except that present in solution was changed to potassium penta-calcium sulfate, while in Tests 7 and 8 it has been assumed that syngenite was the only solid formed.

It is possible, however, that there was slight admixture of syngenite in the first case, and of the penta-salt in the other, due to part of the solid phase being so coated over as not to be in contact with the final solution.

The solid phases in these tests were separated and analyzed. The analyses, together with the theoretical composition of syngenite and potassium penta-calcium sulfate, are given in Table III.

TABLE III

TEST	1	2	Potassium Penta-Calcium Sulfate	7	8	Syngenite
CaO........	30.78	29.56	32.10	17.70	17.30	17.06
K_2O........	11.42	11.22	10.80	26.80	27.04	28.70
SO_3........	54.40	53.80	55.00	49.92	49.92	48.73

Even though the above analyses indicate that in Tests 1 and 2 the solid phase contained some syngenite, and in Tests 7 and 8 some penta-salt, the results from the other tests make it quite evident that the final concentration in the first two tests was considerably below that required for equilibrium, while the final concentration in the last two tests was above the equilibrium point.

In Tests 3, 4, 5, and 6 the conditions were such that equilibrium should have been reached. These results indicate, therefore, that the concentration of potassium sulfate for the equilibrium of potassium penta-calcium sulfate and syngenite with the solution would lie between 7.1 and 10.9 g. per 100 g. of H_2O, and would probably be about 9.5 g. per 100 g. H_2O, this latter value being the average of the results from Tests 3, 4, 5, and 6.

Accordingly, Tests 9, 10, 11, and 12 were so made as to approach this equilibrium concentration both from a low and a high potassium sulfate concentration. The data for these tests show that equilibrium was reached in each case and the concentration of potassium sulfate in the final solution would, therefore, correspond to equilibrium condition.

Taking the mean of the analyses it is seen that these equilibrium concentrations were as follows:

8.95 g. K_2SO_4 per 100 g. of H_2O

or

8.21 g. K_2SO_4 per 100 g. of solution.

The corresponding calcium sulfate concentrations were

0.107 g. $CaSO_4$ per 100 g. H_2O

or

0.100 g. $CaSO_4$ per 100 g. solution.

Calculating these results to moles per 100 moles of water gives

9.26 moles K_2SO_4 per 1000 moles of H_2O

and

0.142 mole $CaSO_4$ per 1000 moles of H_2O.

The figure obtained for the potassium sulfate concentration is considerably lower than would be expected from the data given by D'Ans as is shown by the following table,[1] which gives the equilibrium concentration of potassium sulfate in solution in contact with solid syngenite and potassium penta-calcium sulfate at different temperatures:

Temp.	Moles K_2SO_4 per 1000 moles H_2O
40	4.4
60	6.8
83	9.9

Thus the figure obtained at 100° C., 9.26 moles of K_2SO_4, is less than that given by D'Ans at 83° C.

The figures obtained for the potassium sulfate concentration at 100° C., both for the syngenite and the potassium penta-calcium sulfate equilibrium, have been added to the original diagram of D'Ans and his curves extended to these two points by dotted lines (Fig. 1).

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[1] *Loc. cit.*

[1] THIS JOURNAL, **11** (1919), 4, 329.

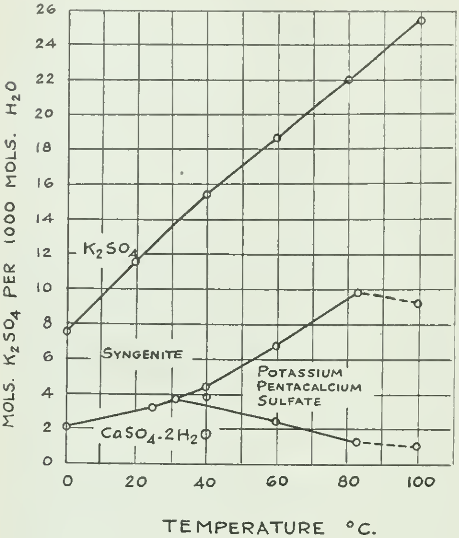

Fig 1

The aim in the tests just described has not been to attain the accuracy that is necessary in proper and exact equilibrium determinations since neither time nor apparatus were available, but rather to obtain results that could be used in practice. It is safe to assume, however, that the figures given for the equilibrium concentration of potassium sulfate are very near the true value. The results obtained, therefore, indicate that the value given by D'Ans for 83° C. is high, or else that the equilibrium curve has a maximum between 83° and 100° C.

SUMMARY

Tests made to determine the equilibrium concentration of potassium sulfate in solution in contact with solid gypsum and potassium penta-calcium sulfate on the one hand and solid syngenite and potassium penta-calcium sulfate on the other at 100° C. indicate that these concentrations are:

1.05 moles of K_2SO_4 per 1000 moles H_2O for the former and 9.26 moles of K_2SO_4 per 1000 moles H_2O for the latter equilibrium.

The corresponding values for calcium sulfate are:

0.24 and 0.10 mole, respectively, per 1000 moles H_2O.

THE STABILITY OF TETRYL[1]

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During the war, when tetryl was being manufactured in great quantities for use in high explosive shell, the question of its stability was almost continually under discussion. Due to the general belief that the treatment of organic nitro compounds with alkalies is bad practice, a clause in the Ordnance Department specifications for tetryl stated that the compound must be stabilized by means of water washing alone.

Up to this time it had been the custom of the du Pont Company to remove the last traces of acidity and other impurities from tetryl by means of a dilute sodium carbonate boil. This method had been found very satisfactory and reduced materially the time required for stabilization. On account of the objections of the Ordnance Department to the use of alkali, however, during the year 1917 the du Pont Company carried out at their Eastern Laboratory a thorough investigation of the stability of tetryl including the causes of instability in crude material and the effect of alkalies on these impurities and upon the tetryl itself.

GENERAL METHODS OF PREPARATION

Tetryl may be prepared by a large number of methods, several of which are of commercial importance. The only one used to any considerable extent, however, is that depending on the nitration of dimethylaniline by means of sulfuric and nitric acids. The tetryl studied throughout our investigation was prepared in this manner.

MOST COMMON IMPURITIES

The impurities most frequently found in tetryl may be divided into the following classes: first, lower or higher nitrated dimethylanilines, and second, impurities in the dimethylanilines used or compounds formed from the nitration of these impurities. The possibility of the presence of sodium picrate and picric acid should also be considered, since it has long been known that tetryl is hydrolyzed to a slight extent to picric acid by means of water alone. When sodium carbonate is used for stabilization, an appreciable quantity of sodium picrate may be formed.

From a search of the literature we concluded that some penta-nitrated material might be present in our tetryl, brought about by the substitution of a nitro group in the *m*-position on the benzene ring. In most cases in which an aniline or phenol has the *m*-position substituted by a nitro group, this group is very mobile and the molecule consequently unstable. It was also found that in exceptional cases dimethylaniline might be nitrated to the penta stage in such a way that the *m*-hydrogen would be replaced by an NO_2 group. This tetranitrophenylmethylnitramine gives on hydrolysis with water trinitromethylnitramidophenol, the *m*-nitro group being replaced by the hydroxyl radical.

On boiling samples of our tetryl with water in the laboratory for stabilization purposes, it was noticed that in most cases the wash water became deeply colored and often showed some acidity even after the acid had previously been completely removed from the tetryl sample. On evaporating these liquors nearly to dryness, a colorless crystalline compound was obtained which was easily identified as trinitromethylnitramidophenol, the hydroxyl group being in the *m*-position to the nitramido radical, m. p. 187° C. This indicated at once the presence of tetranitrophenylmethylnitramine in our tetryl.

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[1] Presented at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

Because of the relatively small quantities of material which could be obtained in this way, it was thought advisable to prepare a sample of the pure tetranitrophenylmethylnitramine—hereafter called *m*-nitro-tetryl—and to carefully determine its properties, stability, etc. A few hundred grams of the material were prepared by nitrating dimethylaniline to the mono-stage, separating the *m*- and *p*-isomers, and nitrating the former to the penta-nitro derivative. The pure compound melts at 146° C. On boiling with water, *m*-nitro-tetryl was hydrolyzed to soluble trinitromethylnitramidophenol and this compound was found to be identical with that recovered from our tetryl wash waters on evaporation. In a similar way sodium carbonate reacts with *m*-nitro-tetryl, and in this case not only is the *m*-nitro group replaced, but the entire methylnitramido radical is removed with the substitution of a second ONa group, giving the di-sodium salt of styphnic acid which is very soluble in aqueous solutions. In the presence of moisture nitrous acid gas is evolved which is very objectionable for a high explosive compound.

It is possible that some *m*-nitro-tetryl in tetryl may be formed from nitration of the dimethylaniline, the group meta to the side chain being substituted during the early stages of nitration. It was thought more probable, however, that the chief source of *m*-nitro-tetryl was the monomethylaniline present in the dimethylaniline used. In order to definitely determine this point, mixtures of methyl and dimethylanilines were nitrated to tetryl. It was found that the per cent of *m*-nitro-tetryl formed varied directly as the monomethylaniline content of the mixture nitrated. Moreover, it was found that by our method of nitration, tetryl prepared from pure dimethylaniline contained no *m*-nitro-tetryl.

CAUSES OF INSTABILITY IN TETRYL

From the reactions of *m*-nitro-tetryl, we felt sure that the instability of our crude tetryl was largely due to the presence of this compound. Its mobile *m*-nitro group, and the ease of formation of nitrous acid would tend to decrease the stability materially. Moreover, with water, it forms a soluble compound, developing at once traces of acidity. However, in order to determine accurately the effect of traces of *m*-nitro-tetryl on the stability and sensitiveness of tetryl, mixtures were made up and tests for stability and sensitiveness made.

In making tests on a great many samples of tetryl, it was noticed that the stability of the material, as shown by the ordinary stability tests depending on the coloration of a test paper, bore no relation to the physical properties of the tetryl. The advisability of using tests of this sort for nitro-aromatic compounds has been questioned for some time. Especially in the case of the Abel heat test, which has attained a much wider use than it deserves, the sensitiveness is so great that the slightest trace of foreign material, moisture, or acidity serves to discolor the test paper.

In order to determine the relative stability of various samples of tetryl and mixtures it was imperative that a quantitative test be developed. For this purpose, the Obermüller or gas evolution test *in vacuo* seemed to offer some possibilities. It was carefully investigated and with slight alterations proved to be of great value in determining quantitatively the gas evolved per hour by explosives at various temperatures.

A few runs with this modified apparatus were sufficient to demonstrate that the purity of tetryl is indicated by its melting point and bears no relation to the heat test. 5 g. samples of tetryl in our Obermüller test apparatus gave from 14.0 to 153 mm. increase in pressure per hour depending on the purity of the product. These samples showed melting points of 129.2° C. to 121.8° C.

In order to determine the sensitiveness of tetryl and its mixtures, an ordinary small drop-test machine was employed. Pure tetryl shows a drop test of 4 oz. at 14 in.

The addition of 10 per cent *m*-nitro-tetryl to tetryl melting at 128.6° was found to lower the melting point to 124.6° C. Smaller quantities caused corresponding depressions. Since it has already been shown that the stability of tetryl is indicated by its melting point, the effect of *m*-nitro-tetryl on the stability is at once shown.

Moreover, the Abel heat test, although unreliable, indicates that the presence of *m*-nitro-tetryl greatly lowers the stability of tetryl. When one per cent of *m*-nitro-tetryl is added to a sample of tetryl having a heat test of 25 min., this is lowered to 15 min., while the addition of 10 per cent gives a mixture with a 3 min. heat test. Pure *m*-nitro-tetryl has a heat test of but one minute.

The addition of small quantities of *m*-nitro-tetryl to tetryl greatly increases the rate of decomposition under vacuum. *m*-Nitro-tetryl itself *in vacuo* gives an increase in pressure of 588 mm. per hr., while ordinary commercial tetryl gives but 20–30 mm., showing that a *m*-nitro-tetryl decomposes approximately 25 times as fast as pure tetryl.

Since it has been found by previous practice that tetryl could be easily purified by means of sodium carbonate, it was thought advisable to determine the effect of this reagent on *m*-nitro-tetryl and on tetryl itself.

A small sample of pure *m*-nitro-tetryl went into solution at once when boiled with dilute sodium carbonate. On evaporating and acidifying the liquor, colorless needles of styphnic acid, melting at 174°, were obtained. The hydroxyl groups are in the 1- and 3-position, both the *m*-nitro and the methylnitramido groups having been hydrolyzed off. On account of the rapidity of this reaction and the solubility of the disodium salt of styphnic acid, this method of removing *m*-nitro-tetryl appears to be almost ideal. As mentioned above, *m*-nitro-tetryl is converted by water alone into soluble trinitromethylnitramidophenol, but the reaction proceeds much more slowly than when sodium carbonate is used and is therefore less satisfactory for purifying tetryl.

ACTION OF SODIUM CARBONATE ON TETRYL

Having proved that *m*-nitro-tetryl may be satisfactorily removed from tetryl by means of sodium carbonate, it appeared advisable to determine the effect of this alkali on tetryl itself. After a thorough laboratory investigation it was shown conclusively that sodium picrate was the sole reaction product when sodium carbonate acted on tetryl.

During the reaction the whole nitromethylamine radical is replaced by the ONa group, nitrous acid being evolved. As might be expected, this reaction takes place to a greater extent on boiling tetryl with caustic alkalies, sodium or potassium picrate being formed with the liberation of methylamine. With sodium carbonate solutions the rate of hydrolysis of tetryl is relatively slow. However, sufficient sodium picrate was prepared in this manner to carefully study its properties and prove its identity. The picric acid after acidification and recrystallization melted at 122.5° C. and showed a molecular weight of 129, the theory for picric acid.

DETECTION OF SODIUM PICRATE IN TETRYL

Since sodium picrate is very soluble in water, it appears that any of this compound formed would be easily removed by the subsequent water washes after neutralization. To settle this point, a sensitive test for the determination of small quantities of sodium picrate in tetryl was developed and it was found that none of this product could be detected in our finished tetryl nor in our second wash water after the alkali boil. This indicated that any sodium picrate formed was removed by the first water wash.

EFFECT OF SODIUM PICRATE ON STABILITY OF TETRYL

Since sodium picrate is a relatively stable explosive, it is difficult to conceive of its lowering the stability of tetryl and its complete removal seems of little importance. Varying mixtures of tetryl and sodium picrate have been carefully made up and the stability and sensitiveness determined. Even large quantities of sodium picrate were found to affect the tetryl but slightly.

The addition of 1 to 10 per cent sodium picrate to tetryl has no effect on the drop test, the mixture giving a detonation in each case with a 4 oz. weight at 14 in., the drop test for pure tetryl. Pure sodium picrate cannot be detonated with an 8 oz. weight at 24 in.

The addition of 10 per cent of picrate to tetryl was found to lower the melting point by only 0.6° C., while the presence of smaller amounts could hardly be detected from the drop in melting point, indicating that the stability of the material was not impaired.

Moreover, the stability of mixtures of sodium picrate and tetryl gave approximately the same gas evolution test as pure tetryl. The decomposition *in vacuo* of a mixture containing 10 per cent sodium picrate was less than that for ordinary crude tetryl.

CONCLUSIONS

It is hoped that this discussion of the stability of tetryl has brought out the following points, most of which have been under more or less discussion since the outbreak of the war.

I—As an indication of the stability of tetryl, ordinary qualitative heat tests are of little value.

II—The Obermüller or gas evolution test *in vacuo* shows the true stability of tetryl to be indicated by the melting point, to which it is directly proportional.

III—The instability of ordinary tetryl is due to a large extent to the presence of tetranitrophenylmethylnitramine (*m*-nitro-tetryl). This impurity is formed by nitration of the monomethylaniline present in the dimethylaniline used.

IV—The nitration of pure dimethylaniline under ordinary conditions gives no *m*-nitro-tetryl.

V—*m*-Nitro-tetryl is unstable and its presence greatly decreases the stability of tetryl.

VI—*m*-Nitro-tetryl may be removed from tetryl by boiling with water, by which it is converted into soluble trinitromethylnitramidophenol, and more readily by a sodium carbonate solution, whereby the soluble sodium salt of styphnic acid (trinitroresorcinol) is formed.

VII—Tetryl is slightly hydrolyzed by a dilute sodium carbonate solution to sodium picrate.

VIII—Sodium picrate is insensitive and stable and its presence does not lower the stability of tetryl to any appreciable degree.

IX—Sodium carbonate is a very satisfactory stabilizing agent for tetryl. It removes acidity and such impurities as *m*-nitro-tetryl. Any sodium picrate formed and not removed by washing is non-injurious to the tetryl.

THE MANUFACTURE OF TRINITROXYLENE FOR USE AS A SUBSTITUTE FOR TNT IN BURSTING CHARGES FOR HIGH EXPLOSIVE SHELL[1]

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From its physical properties trinitroxylene, or TNX, would appear to be most unfavorable for use as the bursting charge for high explosive shell. The melting point of the predominating isomer is very high, 182° C., making it impossible to load by direct casting. Moreover, this compound is almost insoluble in other lower melting nitro bodies at low temperatures such as are preferable for casting, seemingly precluding the casting of such a mixture. It has not more than 80 per cent the explosive strength of TNT, and it is much less sensitive to detonation. The acute situation which developed in the TNT supply in the summer of 1917, however, made it necessary to consider the use even of materials which appeared unfavorable. About this time it was suggested by a member of the du Pont Company's chemical department that TNX might be used to advantage as a partial substitute for TNT by casting a mixture of TNX suspended in molten TNT.

Experiments were immediately started at the Eastern Laboratory for the preparation of a few pounds of TNX for experimental purposes. The nitration process itself offered many difficulties, but a few pounds were prepared, and a study made of the use of the compound in a shell bursting charge.

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[1] Presented at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

Rather to the surprise of those concerned, TNX proved to be almost ideal for the purpose. When 30 to 50 parts of TNX were suspended in 70 to 50 parts of TNT at 100° C. a sufficiently fluid mass was obtained to admit of direct casting without the use of any extruding mechanism. The castings when cooled proved to be completely amorphous, resembling paraffin in texture. They showed no segregation of either component of the charge, were remarkably free from air holes, showed high and uniform densities, were non-hygroscopic, and showed no tendency to become oily or leaky, even on storage at elevated temperatures. They could be completely detonated with smaller primers of tetryl than could castings of TNT alone. They could be drilled with ease for booster cavities, and in fragmentation tests showed results approaching those obtained with refined TNT. Added to these advantages, it was found that more satisfactory castings could be obtained with a mixture of crude TNX and crude TNT than with refined materials, which in itself would produce a considerable saving in both operating and material costs.

Since the potential supply of xylene in the country was at least 20 per cent of the supply of toluene, the development of a manufacturing process for TNX was immediately advisable and the study was at once undertaken.

The development of the manufacturing process from the laboratory scale to the design, construction, and operation of a large scale plant occupied more than a year and a half, and production was proceeding rapidly at the time of the signing of the armistice.

The details of the work done during this period are manifestly beyond the scope of this paper. It will be attempted, therefore, only to outline the difficulties encountered and the methods used in surmounting them.

Ordinary commercial xylene, boiling within a range of 4° to 5° C., contains the three possible isomers, the amounts present varying with the source of the xylene. In general, it appears that such material contains 60 to 70 per cent *m*-xylene, the remainder being made up of *o*- and *p*-xylene with some ethylbenzene and usually small percentages of paraffins and naphthenes.

All of the xylene isomers give trinitro derivatives, though it would naturally be expected that the *o*- and *p*-xylenes would nitrate to that stage with difficulty. The high melting trinitro-*m*-xylene is difficultly soluble in the other isomers, so in the nitration of the mixture we should expect to obtain a final product containing crystals of trinitro-*m*-xylene together with lesser amounts of an oil of lower nitrogen content, composed of the various di- and tri-nitrated isomers. In the preliminary experiments, using commercial xylene, this condition was found to hold. The efficient production of a non-homogeneous material of this type appeared impractical for the following reasons:

1—The control of the final stage of the nitration was difficult owing to the viscous nature of the charge in the nitrator.

2—It was necessary to separate the crystalline product from the spent acid by filtration, followed by a secondary separation of the oily products not held by the filter.

3—The yield of desirable product was greatly lowered owing to the loss of material in the form of oil, which obviously could not be used in shell loading.

4—When washing the oil-contaminated crystals with boiling water in the neutralizing process, there was a tendency for the crystals to cement together in small lumps, which included small quantities of acid from the wash waters. This acid could be finally removed only with great difficulty.

The first requirement was therefore the production of a homogeneous material, and for this three methods of procedure were open: first, by using pure *m*-xylene; second, by increasing the severity of nitrating conditions to the point of partial oxidation of the *o*- and *p*-isomers and more complete nitration of the unoxidized residue; and third, by controlling the composition of the raw material so as to partially exclude the undesirable isomers.

THE NITRATION OF PURE *m*-XYLENE

Pure *m*-xylene is easily prepared by the partial sulfonation of the mixed xylenes, followed by steam distillation of the sulfonated product for the regeneration of the *m*-xylene.

m-Xylene thus prepared, having a boiling range of 0.4° C., was subjected to a three-stage nitration and gave an almost pure trinitroxylene melting above 175° C. It was found, however, that the solid product was precipitated in the final nitration in a very finely divided crystalline form that made the charge extremely viscous. This could not be overcome except by using prohibitive amounts of nitrating acid to obtain the necessary fluidity. Also, as before mentioned, it was found that pure TNX of this character could not be used in castings to as good advantage as the crude material, and the use of pure *m*-xylene was therefore abandoned.

NITRATION OF THE MIXED ISOMERS

The study of the nitration of the mixed isomers was continued while the foregoing work was in progress, and the following methods developed:

The xylene was nitrated in three stages, separation of spent acid being made after each stage. The mononitration was carried out by adding to the xylene at 55° to 60° C. 2$^1/_2$ parts of a nitrating acid containing 38 per cent HNO_3, 52 per cent H_2SO_4, and 10 per cent water, followed by a brief period of agitation. The bi-nitration was made by adding the same ratio of the same mixed acid to the mono-nitrated oil at 80° C. The tri-nitration was carried out by adding the acid bi-nitrated oil to 4 parts (based on xylene) of a mixed acid containing 25 per cent HNO_3 and 75 per cent H_2SO_4 at 90° C., followed by a continued agitation at 95° to 105° C. This method was used both on the laboratory and the semi-works scale with good results. It gave a homogeneous product, and one of sufficiently large crystal structure for convenient filtration and handling. With the xylene in use at the time, however, satisfactory neutralization of the TNX could not be obtained owing to the previously mentioned cementing together of the crystals on the treatment with hot water and consequent inclusion of acid. This was doubtless due to the high content of isomeric compounds.

STUDY OF RAW MATERIALS

In order to overcome this difficulty a study was made of the rectification of solvent naphtha, and of the results obtained by nitration of various ranges of the xylene fraction. Rectifications for this purpose were first carried out at the Deepwater Point Works of the du Pont Company, and later at the Frankford plant of the Barrett Company. The Barrett Company coöperated in all the later portions of this study, and the successful outcome of the work was in large measure due to their assistance in settling this very vital phase of the problem.

A comparison of the physical properties of xylenes from different portions of the range with the results obtained on nitration brought out the following points:

1—The boiling range and specific gravity of the xylene do not offer a satisfactory control of the character of the raw material, and the final value of the xylene for use in the manufacture of TNX can be established with satisfaction only by a nitration test carried out in a manner comparable with the plant method.

2—In general, TNX of the most satisfactory freezing point and in the best yields, is obtained from a xylene meeting the following boiling point specifications:

Range, 1st drop to flask dry 3° C.
First drop, between 137.2° and 139.2° C.
Flask dry, between 138.5° and 140.5° C.

3—Xylenes taken from the *p*-xylene range will nitrate satisfactorily and give good freezing points, but yields will be low.

4—Xylenes taken from the *o*-range, *i. e.*, high in *o*-xylene, will give difficulty in nitration, with low yield and freezing point of product.

5—TNX samples having freezing points of 161.5° C. or better showed no tendency to agglomeration of crystals when treated with hot water. They could be neutralized without difficulty.

In addition to the above points, it was found that the value of a xylene for the preparation of TNX depended in large measure upon the source of the xylene; for example, the coke-oven by-product xylene always gave a more satisfactory TNX than xylene with an identical boiling range from other sources, such as water-gas tar, or drip oil. No satisfactory explanation has been found for this. Water-gas xylene and drip-oil xylene as a rule contain relatively high percentages of hydrocarbons (members of the paraffin and naphthene series, and usually designated "paraffins" for convenience) which resist sulfonation and nitration, and for a time these compounds were considered responsible. However, on isolation of these compounds from water-gas xylene by sulfonation of the xylenes and separation of the unsulfonated residue, followed by nitration of mixtures of this material and coke-oven xylene, there was no effect shown on the freezing point of the resulting TNX, and no greater effect on yield was shown than could be accounted for by the actual "paraffins" added.

On the other hand, when water-gas xylenes of similar properties, but with varying "paraffin" contents, were nitrated, there was a reduction in freezing point of TNX approximately proportional to the "paraffin" content, and a reduction in yield greater than could be explained on the ground of "paraffins" alone.

These results apparently indicate that "paraffins" are not responsible for the difference between coke-oven and water-gas xylene, and possibly indicate the presence of unidentified compounds in the water-gas xylenes other than "paraffins," but appearing coincidentally with them.

LARGE SCALE OPERATIONS

As soon as progress had been made on the subject of specifications for the raw material, active operation was started in a semi-works plant constructed for the purpose, and it was here demonstrated that xylene of the type specified gave satisfaction on the larger scale operation. Final data were also obtained in this work for the design of a large scale plant, and construction of this plant, with a potential capacity of 3,000,000 lbs. TNX per month, was at once started.

The first unit was completed August 1, 1918, and operations were started at once, and at the time of the signing of the armistice two of the five units were in full production of a satisfactory product, with the other units nearing completion or in partial operation.

NOTES ON DOUBLE POLARIZATION METHODS FOR THE DETERMINATION OF SUCROSE AND A SUGGESTED NEW METHOD

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Received August 30, 1919

The well-known principles and methods of double polarization applied in the analysis of commercial sugar products need not be detailed here. The methods in use depend on the assumption that the change in optical rotation of a sugar solution, which is the measure of the sucrose, is the result of the inversion of the sucrose only. One of the chief objections to the original method of Clerget and Herzfeld arises from the fact that the direct reading is made on a practically neutral solution and the invert reading on a strongly acidulated one. Much work has been done in developing improved methods of procedure to prevent or at least mitigate the errors which are introduced under these conditions, especially in sugar estimations of low-grade products where the change in acidity causes changes in the optical rotation of the sugars, other than sucrose, which are present. Those who are interested in these investigations may be referred to the voluminous and familiar papers of Pellet, Sidersky, Anderlik, and others. As the field has by no means been exhausted, even so far as to develop methods which really meet many of the requirements of commercial analysis and general research, the present paper is published as suggestive of a new line of attack of the problem.

In making up the solutions two lots of commercial granulated sugar were used—one from the Standard Refinery of Boston, polarizing 99.95, and the other from the Revere Refinery, polarizing 99.99. The factors of inversion for these sugars were obtained by the Clerget method, modified by carrying out the inversion at room temperature, and by the method of Herzfeld, likewise modified. Table I gives these factors (see also Table II).

TABLE I

METHOD	SUGAR USED	TIME HRS.	TEMPERATURE °C.	FACTOR
Clerget	Std. Granulated	22.0	23	144.56
	Revere Granulated	22.0	28	144.17
			AVERAGE	144.37
Herzfeld	Std. Granulated	21.5	28	142.43
	Revere Granulated	21.5	28	142.67
			AVERAGE	142.56

It is well known that the factor obtained by the invertase method of Hudson is much lower than that obtained by the Clerget and similar procedures, and it is also known that this is caused by the fact that the acid augments the invert reading. What does not seem to be so well known, if it has been published at all, is that *neutralized* acid-inverted solutions give larger readings than the original acid solutions. Apparently neutralization does not affect the increase in rotation caused by the acid, but the reading is still further increased by the salts formed in neutralization as shown in Table II.

TABLE II
(Method of Herzfeld)

TEST	FACTOR FOR— ACID SOLUTION	FACTOR FOR— NEUTRALIZED SOLUTION	DIFFERENCE
1	142.43	143.30	0.87
2	142.69	143.39	0.70
3	142.66	143.41	0.75
		AVERAGE	0.77

An invert-sugar solution, made by heating a $N/2$ (saccharimetric) sucrose solution with 0.01 normal hydrochloric acid on a boiling water bath for 30 min., gave the factor 141.7, agreeing with that given by Browne for a neutral solution, as was to be expected, since the acidity was negligible. Adding hydrochloric acid in the proportion used in the Herzfeld method increased the reading by —1.35. Addition of the equivalent amount of sodium hydroxide to produce a neutral solution, gave a further increase of —0.60.

Some work was done with the modification of Anderlik, in which urea is used as a retardant of the inversion when the direct reading is made in the presence of the usual amount of hydrochloric acid. Our experience with this method on cane products was unsatisfactory, as the direct polarization changed rapidly and indeed was quite unmanageable when the temperature approached 26°. This method, therefore, would be inapplicable in raw-sugar work in the tropics, however satisfactory it may be for low-grade beet products. Our tabulated results, which are not given here since the method has already been adversely criticized by Browne and others, show that unless the direct polarization is completed in less than 3 min. the error from inversion change is too great to be negligible. Glycocoll as a substitute for urea proved still more unsatisfactory.

INVERSIONS WITH MONO- AND TRICHLOROACETIC ACID

It seemed desirable to find a substitute for hydrochloric acid which would invert so slowly at ordinary temperatures as to permit direct readings without error, and yet be sufficiently acid to effect complete inversion upon convenient heat treatment. Accordingly, the following investigations were made with mono- and trichloroacetic acids, which had the great advantage of giving no troublesome precipitate with the soluble lead salts which were left after clarifying. The affinity constant of trichloroacetic acid is given as 75.4 and that of the monochloroacetic acid as 4.8, on the basis of HCl = 100.

TABLE III
DIRECT SACCHARIMETER READING

WITH 0.5 G. TRICHLOROACETIC ACID Time Min.	Reading	Temperature °C.	WITH 0.5 G. MONOCHLOROACETIC ACID Time Min.	Reading
3	50.00	19.2	5	50.00
5	50.00	19.3	6	50.00
7	50.00	19.4	8	50.00
10	50.00	19.6	10	50.00
15	50.00	19.3	15	50.00
20	49.90	20.4	20	50.00
30	49.75	20.6	30	50.00
40	49.70	20.9	45	49.85
60	49.55	21.4	60	49.80
90	49.30	21.6	25 hrs.	47.50

(13.0 g. of sucrose in 100 cc.)

The first series of experiments (Table III) was to determine the rates and factors of inversion at ordinary temperatures of half (sugar) normal solutions of sucrose, containing 0.5 g. of mono- and trichloroacetic acids, respectively. These two solutions were heated in stoppered flasks for 30 min. in a boiling water bath, and inverted smoothly without discoloration, giving constants of 142.2 in both cases.

TABLE IV—EFFECT OF ACETATES ON INVERSION FACTOR OF A $N/2$ (SACCHARIMETRIC) SOLUTION OF SUCROSE INVERTED BY 3 G. OF MONOCHLOROACETIC ACID AT 100° C.

Sodium Acetate per 100 Cc. G.	Time of Heating Min.	Average Value Inversion Factor	No. of Observations
None	30	141.02	10
0.0625	30	141.00	5
0.125	30	141.05	4
0.325	30	141.10	1
0.500	30	141.00	5
0.625	30	140.32	4
0.625	60	141.06	3

These inversions of pure sucrose solutions of commercial concentration promised a satisfactory method, but Tolman's observations on citric acid inversions have shown that soluble acetates have a marked inhibitory effect. It was calculated that 1 cc. of lead acetate (sp. gr. 1.26) would leave soluble acetate equivalent to 0.125 g. of sodium acetate. A half (sugar) normal solution of sucrose was therefore made up with 0.5 g. of monochloroacetic acid and 0.625 g. of sodium acetate, the latter equivalent to 5 cc. of lead acetate, which was considered a maximum for all ordinary commercial polarizations. It was found that acetate in this amount retarded inversion in the cold to such an extent that there was no change in the

TABLE V—LAG OF POLARIZATION OF VARIOUS INVERTED SUGAR SOLUTIONS

A			B			C			D			E		
Time Min.	Reading	Temp. Deg.	Time Min.	Reading	Temp. Deg.	Time Min.	Reading	Temp. Deg.	Time Min.	Reading	Temp. Deg.	Time Min.	Reading	Temp Deg.
6	11.50	18.6	7	13.50	19.8	5	12.00	19.4	6	13.60	22.1	3	12.70	21.4
7	12.20	18.8	8	13.90	19.8	6	12.75	19.5	10	14.10	22.4	4	13.25	21.5
9	13.00	19.7	9	14.30	20.0	8	13.60	20.0	15	14 30	22.4	5	13.55	21.7
10	13 15	20.2	10	14.50	20.3	10	14.20	20.4	27	14.85	22.6	7	14.05	22.2
12.5	13.50	21.0	12	14.70	20.8	15	14.85	20.8	40	14.70	23.6	14	14.35	22.6
									Hrs.					
15	13.80	21.4	15	14.85	21.3	20	14.95	21.2	23	15.80	20.0	25	14.50	23.2
30	14.15	21.4	20	14.90	21.6	30	14.85	21.7				40	14.50	23.5
												Hrs.		
60	14.40	23.2	30	14.80	22.0	100	15.35	22.0				2.25	14.50	23.5
			Hrs.			Hrs.								
75	14.30	23.0	20	15.85	20.0	18	16.10	20.0				4	15.10	23.6
100	14.00											24	15.76	20.0
Hrs.														
20	15.20													

A—$N/2$ Sucrose solution inverted by 0.01 per cent HCl at 100°.
B—$N/2$ Sucrose solution inverted by 0.01 normal HCl at 100°.
C—$N/2$ Sucrose solution inverted by 0.5 g. trichloroacetic acid at 100°.
D—$N/2$ Sucrose solution inverted by 3 g. monochloroacetic acid with 0.625 g. of $NaC_2H_3O_2$.
E—$N/2$ Sucrose solution inverted by 3 g. monocbloroacetic acid and 0.625 g. of $NaC_2H_3O_2$.

direct reading for several hours, and even 30 min. treatment at 100° gave only 15 per cent inversion. The retarding influence of the soluble acetate could be overcome by increasing the amount of chloroacetic acid, but in the case of trichloroacetic acid this was not practicable because, if enough acid was used to complete the inversion of a $N/2$ solution, it gave a reading of 49.90 after only 4 min. in the cold.

Two grams of the trichloro-acid in the presence of 0.625 g. of soluble acetate caused an inversion of only 94.3 per cent in 30 min., 3 g. being necessary for complete inversion.

With the soluble acetate omitted, 3 g. of trichloroacetic acid accelerated the inversion in the cold as shown.

$N/2$ solution, polarizing 50.00.

At end of 5 min.	49.85
At end of 10 min.	49.75
At end of 25 min.	49.60

Furthermore, the trichloroacetic acid, decomposing in the water bath, frequently gave off so much chloroform vapor as to burst the flasks. With monochloroacetic acid there is a slight depression of the polarization caused by the addition of the acid and acetate, as a similar $N/2$ sugar solution at the end of 2 min. gave a reading of 49.85 which remained constant through observations of a few minute intervals carried on for over an hour.

A sample of Cuban second sugar, clarified with 2 cc. standard basic lead acetate solution per $N/2$ weight and treated with 3 g. of monochloroacetic acid, gave a constant polarization for over an hour.

To test the effect of an excess of lead acetate clarifier, a $N/2$ sucrose solution to which had been added 1 cc. of lead acetate clarifier, 0.5 g. of sodium acetate, and 3 g. of monochloroacetic acid, was found to resist inversion for 30 min. in the cold but inverted smoothly in the boiling water bath in 30 min. with no signs of discoloration, the inversion factor being identical with that of a lead-free solution similarly treated. Table IV shows the influence of varying amounts of sodium acetate on the inversion factor obtained with monochloroacetic acid. It will be seen that the inversion is incomplete after 30 min. boiling in the presence of more than 0.500 g. of soluble acetate.

To test the effect of sodium chloride two inversions with monochloroacetic acid were made in the way described in the above series, one with 0.625 g. of acetate and 0.65 g. of sodium chloride, the other with 0.65 g. of sodium chloride only. The factors obtained were 141.04 and 141.08, respectively, showing that a sodium chloride content up to 5 per cent of the weight of sample does not affect the inversion.

Whenever sugar solutions are inverted at a high temperature with hydrochloric or monochloroacetic acid there is a noticeable lag in the polarization even after the solution has reached temperature equilibrium with that of the saccharimeter, the constant reading being always (numerically) greater than the initial. This lag, usually lasting but a few minutes, has been repeatedly noticed in solutions treated by the Clerget and Herzfeld methods, and is greater the less the acid content. When $N/100$ HCl was used the initial polarizations were as much as two divisions lower numerically than the final constant value. With chloroacetic acids the lag is smaller but it lasts longer (Table V). The possible causes of this lag will not be discussed at this time.

The factor 141.0 has been adopted as correct for a monochloroacetic acid inversion, and is based on the series of inversions of pure sucrose shown in Table VI. The 60 min. inversions showed some decomposition, as indicated by the lower factor. If, however, low-grade products, requiring as much as 5 cc. of clarifier, are inverted, the time should be increased to 1 hr., owing to the retarding influence of the soluble acetates. This is made clear in Table IV.

TABLE VI—DETERMINATION OF INVERSION FACTORS BY THE MONOCHLOROACETIC ACID METHOD

15 Min.	30 Min.	60 Min.
141.60	141.14	140.30
140.08	140.92	140.38
141.20	140.90	140.40
140.98	140.90	140.20
141.16	141.00	......
Av. 141.20	140.97	140.32

To compare this method with the invertase method of Hudson, accepted as the standard method for accurate results, an invertase solution was prepared from compressed yeast. Half-normal sugar solutions were inverted at about 30° C. with varying amounts of this solution. The results are given in Table VII.

TABLE VII—INVERSION CONSTANTS BY INVERTASE METHOD OF HUDSON

TIME OF INVERSION Hrs.	FACTORS FOR VOLUME OF INVERTASE SOLUTION USED 5 cc.	7.5 cc.	10 cc.
21	140.46	141.54	141.68
45	141.54	141.34	141.72
70	141.70	141.72	. . .

Time permitted only comparative tests by the invertase, Herzfeld and monochloroacetic methods on two samples of Cuba seconds and one of refinery barrel sirup. In the invertase tests the solutions were carefully "deleaded" according to directions by Browne.[1] In the other tests the minimum amount of basic lead acetate to clarify was used. Table VIII shows the comparative results by the three methods, making it clear that the monochloroacetic acid method gives results much closer to those obtained by the standard invertase method than does the Herzfeld method.

TABLE VIII

A—Comparison of Double Polarization Methods

SAMPLE	METHOD	Direct Polarization	Concentration of Solution	Invert Polarization (All Readings in $N/2$ Solution)	Factor Used	Per cent of Sucrose
Cuban Second Sugar No. 1438	Invertase	88.01	N	—14.10	141.70	88.24
	Monochloroacetic	44.44	$N/2$	—13.51	141.00	88.45
	Herzfeld	89.01	N	—14.38	142.66	88.63
Cuban Second Sugar No. 1323	Invertase	88.40	N	—11.18	141.70	84.08
	Monochloroacetic	44.00	$N/2$	—11.26	141.00	84.36
	Herzfeld	88.23	N	—12.16	142.66	85.04
Barrel Sirup from Am. Sug. Rfy.	Invertase	34.63	N	—6.65	141.70	36.35
	Monochloroacetic	17.39	$N/2$	—6.46	141.00	36.41
	Herzfeld	35.02	N	—6.93	142.66	36.85

B—Percentage Difference between Per cent of Sucrose by Three Methods

SAMPLE	Monochloroacetic minus Invertase	Herzfeld minus Invertase	Herzfeld minus Monochloroacetic
Cuban Second No. 1438	0.21	0.39	0.18
Cuban Second No. 1323	0.28	0.96	0.68
Barrel Sirup	0.06	0.50	0.44

The effect of the monochloroacetic acid method on commercial glucose readings was briefly investigated.

Many analysts do not realize that commercial glucose is not a well-defined chemical compound but may vary considerably in composition and physical characteristics. The average glucose of to-day is considerably lower converted than that of a few years ago so that the Ventzke reading of 175 for the (sucrose) normal weight under standard conditions of polarizing is too low. In fact, the sample of glucose used in the present investigation showed a Ventzke reading of 177.85.

TABLE IX—EFFECT OF MONOCHLOROACETIC ACID ON COMMERCIAL GLUCOSE READINGS IN DOUBLE POLARIZATION METHOD

TEST MADE	Readings with no Acid	Readings with 3 g. Monochloroacetic Acid	DIFFERENCE	TOTAL DIFFERENCE
Before heating	(*a*) 88.70	(*b*) 88.10	$(a - b) = 0.60$	1.89
After heating	88.09	(*c*) 86.81	$(b - c) = 1.27$	....
Before heating	(*a*) 88.49	(*b*) 88.05	$(a - b) = 0.44$	1.99
After heating	88.50	(*c*) 86.85	$(b - c) = 1.50$	.
Before heating	(*a*) 88.52	(*b*) 87.98	$(a - b) = 0.54$	1.85
After heating	88.53	(*c*) 86.67	$(b - c) = 1.31$	...
			AVERAGE	1.88

Table IX shows the polarization effect of monochloroacetic acid, as used in the double polarization method described, on an approximately 10 per cent solution of this glucose.[2]

SUMMARY

The following double polarization method is suggested as a result of these investigations. Dissolve the normal weight of sample in a 100 cc. flask, clarify with an appropriate amount of lead acetate, make up to volume and filter (the usual procedure for commercial polarizations). Transfer 50 cc. of filtrate to a 100 cc. flask, add 15 cc. of a 20 per cent solution of monochloroacetic acid, make up to volume with water, and polarize within 15 min. after adding the acid. To invert, transfer about 50 cc. of the solution to a 50 cc. flask, stopper tightly by tying down the cork, and immerse flask in boiling water, maintaining active ebullition for 30 min., or for 60 min. for low-grade products clarified with a large amount of lead acetate. Remove flask, and cool quickly to room temperature. Allow to stand at least 2 hrs. and polarize in a 200 mm. tube with thermometer.

$$S = \frac{2(a - b)}{141 - \frac{t}{2}} \times 100$$

S = Per cent Sucrose b = Invert reading
a = Direct reading t = Temperature

All solutions should be made and polarized as nearly as possible at 20°.

The advantages of this method are:

I—Direct and invert readings are made on a solution of unchanged acidity and sugar concentration.

II—Excess of basic lead acetate, equivalent to one cc. in a half (sugar) normal solution, does not affect the inversion or produce troublesome precipitates.

III—It gives more accurate results than the Herzfeld method.

IV—Inverted solutions of low-grade products are lighter in color than those inverted by the Herzfeld method, and therefore easier to polarize.

V—No error is introduced by making up to volume after inversion.

The chief disadvantage seems to be the time required, but this is less than that required by the invertase or the more rational modifications of the Clerget and Herzfeld methods in which the inversion is carried out at room temperature, which requires at least 22 hrs. The actual time required in manipulation is little, if any, more than that taken by the usual methods.

THE QUANTITIES OF PRESERVATIVES NECESSARY TO INHIBIT AND PREVENT ALCOHOLIC FERMENTATION AND THE GROWTH OF MOLDS[1, 2]

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The practice of preserving perishable foodstuffs for longer or shorter periods is not new. The application of heat and cold are old family methods which

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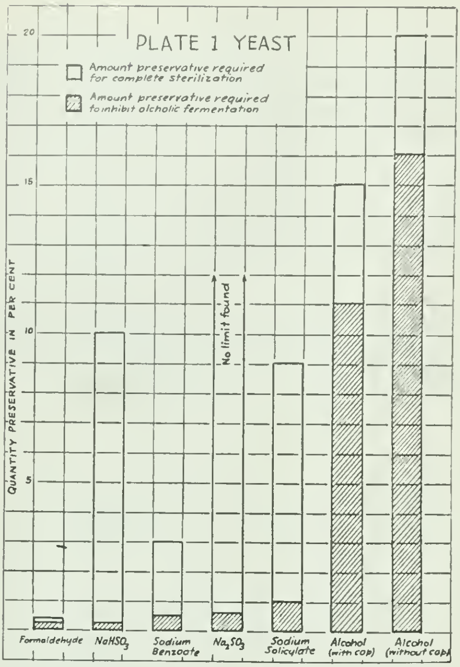
[1] "Handbook of Sugar Analysis," p. 276.

[2] Weber and McPherson's investigations. *J. Am. Chem. Soc.*, **17** (1895), 312, 320.

[1] Abstracted from thesis submitted in partial fulfillment of the requirements for the degree of Master of Arts in Chemistry in the Graduate School of the University of Illinois.

[2] Read at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.



have been elaborated upon and improved in the more modern methods of canning and cold storage. The drying of fish, fruits, and meats, either in the sun or by artificial heat, has been known and utilized for centuries; probably the use of salt is nearly, if not quite, as old. The use of sugar either with or without the addition of vinegar and various spices is but another old family contrivance. The application of creosote from the smoke of incompletely burned wood is thought to have been discovered accidentally in an attempt to use artificial heat in drying. All of these methods, or at least variations of the same principles, are in use today, and in addition we now use certain manufactured chemicals in the preservation of our perishable food materials.

The object of this study was to determine the amount of various food preservatives required to check alcoholic fermentation, to inhibit the decomposition of foodstuffs by molds, and to destroy all living organisms in standard one per cent dextrose broth.

Conditions under which food is kept in the home permit of chance inoculation. Some foods, especially those which are used as condiments, offer a greater opportunity than others for chance inoculation. The work of Bachmann[1] and, to a greater extent, that of Hoffmann and Evans[2] depends partly upon chance inoculation. This affords a probability of a mixed culture, also the possibility of losing some of the preservative by evaporation, especially in the case of volatile preservatives, as will be explained later.

For carefully controlled experiments nothing should be left to chance; in this series of determinations we have used positive inoculation of sterile media with a pure culture of the specific organism. Hence the results give a definite measure of the amount of the preservative necessary for absolute preservation and also for the inhibition of gas formation and the visible growth of mold.

EXPERIMENTAL

The food material used for this work was a 2 per cent dextrose broth.[1] At first we added to 10 cc. of this broth 10 cc. of distilled water, minus the volume of the preservative, autoclaving at 10 lbs. for 10 min. to insure complete sterilization, and then adding the required amount of preservative. Later we found that better results were obtained by sterilizing a known volume of this double concentration broth and adding sterile water and preservative to double the original volume, thus giving a one per cent dextrose broth as a culture media.

After the addition of the preservative, the tubes were allowed to stand for a short time before inoculating with a pure culture of *Saccharomyces cerevisiae*,[2] or the green mold, *Penicillium glaucum*.[3] The cultures were used from 3 to 5 days after transplanting on dextrose agar slants. After inoculation the tubes were allowed to stand at room temperature for a period varying from 4 to 8 days, according to the time required to produce visible growth in the check tubes.

Determinations were made in duplicate and always accompanied by duplicate checks, using 10 cc. of the double concentration broth, adding 10 cc. of sterile distilled water, and inoculating with the specific organism. The tubes showing positive gas formation were considered to have undergone alcoholic fermentation, and in case of no gas formation, agar plates were made to determine, if possible, the point at which the organisms were killed. In the same way plates were made from the tubes showing no visible growth of mold. These plates were allowed to stand at room temperature until the plates made from the check tubes showed a positive growth of the organism with which it had been inoculated.

ABSOLUTE ALCOHOL—In the first set of determinations absolute alcohol was used as the preservative. When the tubes were covered with rubber caps, to eliminate evaporation, the tubes inoculated with *Sacc. cerevisiae* showed gas formation up to a concentration of 11 per cent alcohol;[4] no living organisms were found at 15 per cent. The tubes inoculated with *P. glaucum* showed a visible growth up to 8 per cent and no living organisms were found above 14 per cent. Where no attempt was made to prevent evaporation, *i. e.*, tubes not capped, the results were not uniform and a higher concentration of alcohol was required: 16 per cent to prevent gas formation and 20 per cent to kill *Sacc. cerevisiae;* 8 per cent to prevent visible growth of mold, and 17 per cent to completely destroy *P. glaucum.*

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[1] This Journal, **8** (1916), 620.

[2] *Ibid.*, **3** (1911), 835.

[1] 20 g. of dextrose, 6 g. of meat extract, and 1000 cc. of distilled water were heated on a water bath for 20 min., 10 g. of peptone were then added, the broth filtered, tubed, and autoclaved at 10 lbs. for 10 min.

[2] The culture of *Sacc. cerevisiae* was obtained by plating out from Fleischmann's yeast and isolating a pure culture on a dextrose agar slant.

[3] The culture of *P. glaucum* was obtained by evaporating a known volume of a certain proprietary remedy to a thick sirup, making up to the original volume with distilled water, and allowing this to stand until a growth of mold was obtained. The mold was then plated out and a pure culture isolated on a dextrose agar slant.

[4] Per cent by volume.

SODIUM SALICYLATE—Yeast tubes, to which sodium salicylate[1] had been added, showed gas in one of the one per cent[2] tubes, and a concentration of 9 per cent was necessary to kill the organisms. Sodium salicylate seemed much more efficient as a preservative against molds, as a visible growth of mold was obtained up to a concentration of 3 per cent, and no living organisms were found above 5 per cent concentrations of the salt.

SODIUM BENZOATE—Dextrose broth preserved with sodium benzoate and inoculated with *Sacc. cerevisiae* showed no gas formation beyond 0.5 per cent, and no living organisms were found above 3 per cent. A 5 per cent solution of sodium benzoate was sufficient to kill the *P. glaucum*, and visible growth was absent in 0.25 per cent. According to Held,[3] only a small part of the benzoic acid is utilized as a preservative, as the greater part is bound by the protein of the media; if a stronger acid is used to satisfy this acid binding power of the protein, the effective disinfecting concentration of the benzoic acid is lessened. The disinfecting power seems to be due wholly to free benzoic acid, even when added in the form of salts, although the action is not due to the mere acidity, *i. e.*, the concentration of the hydrogen ion.[4]

SODIUM SULFITE—Yeast tubes containing 0.6 per cent sodium sulfite[5] showed no gas formation, and living organisms were found through 12 per cent; there was a visible growth of *P. glaucum* through a concentration of 12 per cent; no higher concentrations were used.

SODIUM ACID SULFITE—In broth preserved with sodium acid sulfite no gas was formed and no visible growth was found even in a concentration of 0.25 per cent although living mold organisms disappeared only at 6 per cent; and living organisms of *Sacc. cerevisiae* disappeared in tubes containing 10 per cent sodium acid sulfite.

FORMALDEHYDE—Tubes to which formaldehyde[6] had been added showed no gas formation and no living organisms at concentrations as low as 0.25 per cent; no visible growth of *P. glaucum* was found at 0.25 per cent although living organisms were found to persist up to 0.4 per cent.

CONCLUSIONS

Under temperature conditions at which foodstuffs are kept the greater part of the time (room temperature) and under other conditions most favorable to the growth of the specific organisms, *i. e.*, the use of media best fitted to the organism in question, sterilization of media, and inoculation with a pure culture, we obtained the following results which are expressed in both graphic (Plates 1 and 2) and tabular form:

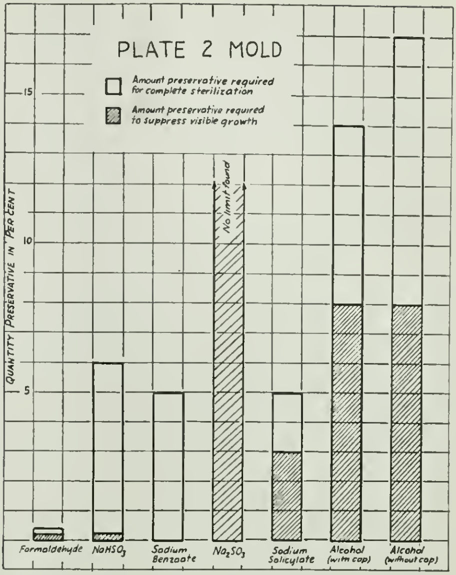

TABLE 1—CONCENTRATIONS NECESSARY TO INHIBIT AND PREVENT GAS FORMATION AND THE GROWTH OF MOLDS

	Saccharomyces cerevisiae		*Penicillium glaucum*	
PRESERVATIVE	GAS FORMATION Per cent	NO LIVING ORGANISMS Per cent	GAS FORMATION Per cent	NO LIVING ORGANISMS Per cent
Alcohol, without cap	16	20	8	17
Alcohol, with cap	11	15	8	14
Sodium salicylate	1	9	3	5
Sodium benzoate	0.5	3	None in 0.25	5
Sodium sulfite	0.6	12% not sufficient	12% not sufficient	12% not sufficient
Sodium acid sulfite	None in 0.25	10	None in 0.25	6
Formaldehyde	None in 0.25	None in 0.25	None in 0.25	0.4

Formaldehyde and sodium acid sulfite exerted the same inhibitive effect toward *Sacc. cerevisiae* and were the most efficient; next in order were sodium benzoate, sodium sulfite, sodium salicylate, and the least efficient of all, alcohol. For absolute sterilization this order did not hold, the most efficient was formaldehyde, then sodium benzoate, sodium salicylate, sodium acid sulfite, alcohol, and sodium sulfite.

There was no visible growth of *P. glaucum* in concentrations as low as 0.25 per cent of sodium acid sulfite, formaldehyde, or sodium benzoate; 3 per cent of sodium salicylate or 8 per cent alcohol were required; 12 per cent of sodium sulfite were not sufficient to inhibit growth. Practically the same order held for complete sterilization: formaldehyde, sodium benzoate, sodium salicylate, sodium acid sulfite, alcohol, and sodium sulfite.

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[1] Percentage purity of sodium salicylate and of sodium benzoate was determined by dissolving a known weight of the salt in distilled water, adding an excess of sulfuric acid, igniting at a low red heat in a platinum crucible, and weighing the sodium sulfate formed.

[2] Per cent by weight.

[3] *Arch. Hyg.*, **84** (1915), 289; *Chem. Abs.*, **10** (1916), 2358.

[4] Marshall, "Microbiology," **1912**, 408.

[5] Percentage purity of sodium sulfite and acid sulfite was determined according to the method outlined by Treadwell-Hall, "Analytical Chemistry," 3rd Ed., **2**, 692.

[6] Concentration of formaldehyde determined by oxidation with iodine in alkaline solution, Romijn's method, as outlined in Sherman's "Organic Analysis," 2nd Ed., 40.

THE EFFECT OF CONCENTRATION ON THE DETERIORATIVE ACTIVITY OF MOLD SPORES IN SUGAR[1]

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It is common knowledge that the reduction of the moisture content of sugar is responsible for a diminution of deterioration. This is tantamount to stating that an increase in concentration of the films surrounding the individual particles in any given mass of sugar produces the same effect. The influence of this factor on the activities of bacteria has been the subject of thorough investigation by Owen.[2] and our recent work[3] with molds has led to the conclusion that "the factor of safety for sugars well infected with molds would appear to be lower than is generally supposed." The full import of such a consideration depends to a considerable degree upon the fact that molds may be responsible for the inversion of sucrose where only spores are present as well as when mycelia are developed. Furthermore, it has been shown[4] that the invertase activity of mold spores is exhibited at concentrations of sugar solutions varying from 10 to 70 per cent, with maximum activity at 50 to 60 per cent. In the same connection it was observed that an increase in the number of mold spores is responsible for increased invertase activity at any definite concentration—including saturated solutions. While these might be considered sufficient grounds for inference regarding the deteriorative activity of mold spores in sugars of known composition, it was deemed advisable to carry out such an investigation on a more practical scale.

Table I—Summary Showing Per Cent Increase in Reducing Sugars in Inoculated Molasses after 4 Months' Incubation

Concentration	*Cladosporium*	*Aspergillus flavus*	*Aspergillus* S. Bain.	*Penicillium expans.*	*Syncephalastrum*	*Aspergillus niger*	Moisture ratio
Blackstrap............	..	..	18.4	9.8	...	4.7	0.44
5/6 B. S. + 1/6 sirup...	5.8	..	19.7	22.3	...	..	0.49
4/6 B. S. + 2/6 sirup...	38.3	12.3	53.2	56.7	...	36.1	0.57
3/6 B. S. + 3/6 sirup...	53.8	33.7	83.6	71.6	9.5	73.6	0.63

A series of sugars with films of known composition were made in the laboratory by coating large crystals of sterilized sugar with sterilized blackstrap molasses and 60° Brix sugar sirup in definite proportions, and purging in the centrifugal, a method previously employed with success.[5] These sugars and corresponding molasses were aseptically inoculated with mold spores by adding 15 g. of sugar containing approximately 1000 spores per g. (prepared as previously described)[6] to 135 g. of sugar in tightly corked Erlenmeyer flasks which were paraffined. The molasses was inoculated with a single scoopful of mold. Solid rubber stoppers, paraffined three times at short intervals, were later used. All flasks were incubated at 28° to 30° C.

In Table I is presented the summary of the per cent increase in reducing sugars over check as resulting from the inoculation of molasses by molds, all values representing the averages of closely agreeing triplicate determinations. These data will appear in greater detail in bulletin form.[1] It will be observed that with each mold used the per cent increase in reducing sugars is made greater with a decrease in concentration of the molasses medium at the end of a 4-month incubation period. There was a corresponding decrease in sucrose Clerget in every sample. While this increase is striking, it does not follow a rigid mathematical progression, due to certain discrepancies which result from such a method of inoculation. It will be seen from Table I that *Aspergillus* Sydowi Bainier and *Aspergillus niger* exhibit the maximum inversion, closely followed by *Penicillium expansum*. This corroborates previous conclusions concerning the deteriorative activity of these organisms both in the mycelial and spore stage.[2]

Since such definite increases were obtained when molasses of known concentrations were used, it might be expected that refined sugar coated with such different molasses would yield similar results. That this is practically the case may be judged from the data in Table II, which represents a summary of the per cent increase in reducing sugars over check as resulting from an inoculation with mold spores at the rate of 100,000 per g after one month's incubation. It will be seen that an increase in moisture ratio

$$\text{M. R.} = \frac{\text{Moisture}}{100 - \text{Polarization}},$$

which means a decrease in concentration, is responsible for raising the per cent increase in reducing sugars in most instances, except where blackstrap films were employed. The latter phenomenon may be accounted for by the fact that the molasses film was relatively thin, due to too prolonged purging. However, the other data, despite negligible discrepancies, are substantial proof of the direct effect of concentration on the deteriorative activity of molds. This has been proven to be a case of true inversion by the fact that an increase in reducing sugars has almost invariably been accompanied by a decrease in sucrose Clerget in the same sample. As in all previous work, *Aspergillus* Sydowi Bainier exhibits the greatest power of inversion.

Table II—Summary Showing Per Cent Increase in Reducing Sugars of Inoculated Sugars after One Month's Incubation

Concentration	*Aspergillus niger*	*Aspergillus* S. Bainier	*Penicillium expansum*	Moisture ratio
Blackstrap............	31.0	142.9	95.2	0.20
4/6 B. S. + 2/6 sirup.....	75.0	195 0	170.0	0.08
5/6 B. S. + 1/6 sirup.....	70.4	270.4	170.4	0.14
3/6 B. S. + 3/6 sirup. ..	95.7	391.1	239.1	0.18
3/6 B. S. + 3/6 sirup. ..	104.6	404 5	218.2	0.20

If the results in Table II are compared with those presented in Table I, it may be noted that there was a greater deteriorative activity revealed in the former case where the moisture ratio was actually much lower. This would seem, upon the surface, to contradict the conclusion that a lowering of the concentration of the medium increases the deteriorative activities of molds. However, it must be remembered that the deteriorative activity of molds in any single medium is a resultant of at least two variables, *i. e.*, concentration and amount of inoculum. We have shown in another paper[1] than an increase in amount of inoculum is responsible for an increase in inversion in any sugar solution of definite concentration. That this principle applies to manufactured sugars is indicated here, for the inoculum used in Table II was approximately 100 times as large as that employed in Table I. Consequently, this experiment shows that a decrease in concentration causes increased deteriorative activity in mold-infected sugars, all other things being equal. Nevertheless, the effect of other variables cannot be overlooked. A similar experiment was repeated over a period of 4 mo. and the data gave similar evidence with moisture ratios varying from 0.18 to 0.29.

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[1] Read at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

[2] Owen, *Louisiana Bulletin*, **162**.

[3] Kopeloff and Kopeloff, *Louisiana Bulletin*, **166** (1919).

[4] Kopeloff and Byall, "The Invertase Activity of Mold Spores as Affected by Concentration and Amount of Inoculum." Read at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919, to appear in *Jour. Agr. Res.*, February 15, 1920.

[5] Owen, *Loc. cit.*

[6] Kopeloff and Kopeloff, "Do Mold Spores Contain Enzymes?" Read at the 57th Meeting of the American Chemical Society, Buffalo, N. Y., April 7 to 11, 1919, and printed in *J. Agr. Res.*, [4] **18** (1919), 195.

[1] Kopeloff, "Biological Factors Affecting the Deterioration of Cane Sugar," *Louisiana Bulletin* (in preparation).

[2] Kopeloff, *et al.*, *Loc. cit.*

Considering the importance of the moisture ratio in predicting the keeping quality of sugar in storage under what is known as the "factor of safety" rule, it is of special interest to note that here is presented evidence of the deterioration of manufactured cane sugars with moisture ratios from 0.08 to 0.29 when sufficiently infected with mold spores; and, furthermore, that this deterioration occurs even in films of the highest concentrations, namely, of blackstrap molasses. In sugar solutions we have already arrived at the resultant effect of the combined variables of concentration and amount of inoculum. In other words, in saturated sugar solutions upwards of 5000 spores per g. are required to effect inversion.[1] We have experiments nearing completion which should establish similar criteria for sugar coated with films of known concentration as herein described. In this way it is our purpose to arrive at a satisfactory method of judging the keeping quality of a sugar from the standpoint of mold infection, which we have shown to be capable of inducing serious economic losses in sugar as a result of its deteriorative activity.

We wish to acknowledge our indebtedness to the Station staff for their kind assistance.

SUMMARY

1—A decrease in concentration of molasses inoculated with molds is responsible for a progressive increase in reducing sugars and a decrease in sucrose Clerget when incubated at 30° C. for 4 mo.

2—A decrease in the concentration of films in inoculated laboratory-made sugars having films of known concentration and moisture ratios of 0.08 to 0.20, caused an increase in reducing sugars (and a decrease in sucrose Clerget) which gave evidence of active deterioration. These sugars were incubated at 30° C. for one month, and similar results followed a like incubation of 4 mo.

3—*Aspergillus* Sydowi Bainier, followed by *Aspergillus niger*, and *Penicillium expansum*, in the order named, effected the greatest deterioration in both molasses and sugar.

4—There is evidence that an increase in inoculum is responsible for an increase in inversion at definite concentration. This investigation with laboratory-made sugars corroborates previous results obtained with sugar solutions.

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[1] Kopeloff and Byall, *Loc. cit.*

THE CAUSE OF DETERIORATION AND SPOILING OF CORN AND CORN MEAL[1]

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Considering the great economic importance of Indian corn in the world's commerce, it is evident that the proper conditions for the preservation of this grain should be well understood and closely adhered to under all circumstances. That such is not the case, however, is shown by the fact that every year thousands of tons of sound corn are subjected to conditions under which the grain deteriorates or spoils during storage in bins or while in transportation in cars or ships. The *American Coöperative Manager* states that the loss to shippers, in four months of one year, through the deterioration of corn arriving in the Chicago market, amounted to more than $4,000,000. It is also well known that tremendous losses are sustained in the exportation of corn to European countries. The problem of keeping meal made from the whole grain of corn in a fresh, sweet state and fit for human consumption has long puzzled both miller and consumer.

Partly as a war measure and also on account of its economical importance in times of peace, an investigation was suggested by the Director of the Kentucky Agricultural Experiment Station, about a year ago, the object of which was to determine the underlying causes of the deterioration and spoiling of corn and corn meal while in the channels of commerce. Thus far our experiments have been confined to the laboratory and were therefore carried out on small portions of material. However, the conditions under which the results have been obtained were so planned as to represent what may be considered a duplication of those under which much larger quantities of corn spoil.

For the experiments in this investigation a quantity of sound and thoroughly air-dry grains of corn of the crop of 1917, which contained 12 per cent of moisture, was selected. This was divided into two equal parts, one of which was ground into meal, the other remaining unground. The unground grains and the meal were further subdivided into 1000-g. lots, each of which was stored separately in glass jars, sealed to exclude air and moisture.

CORN GRAINS

MOISTURE ABSORPTION—For an experiment on the hygroscopic property of corn containing 12 per cent of moisture, 1000 g. of the grains were placed in a porcelain evaporating dish resting on an ordinary "acid dish" partly filled with distilled water, the whole being covered by a bell-jar on a glass plate. A small wedge, about 2 mm. thick, placed between the rim of the bell-jar and the glass plate, provided a small opening for partial ventilation. The dish of corn was weighed at intervals. Table I shows the increase of weight due to moisture absorbed by the air-dry corn from a moist atmosphere.

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[1] An abstract of this paper was read before the Division of Agriculture and Food, 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

TABLE I—ABSORPTION OF MOISTURE BY AIR-DRY CORN GRAINS

	Observed weight G.	Average increase per day G.
Initial wt. of corn (12 per cent moisture)	1000	..
Wt. after 1 day	1008	8
Wt after 2 days	1015	7
Wt. after 3 days	1020	5
Wt. after 4 days	1024	4
Wt. after 5 days	1028	4
Wt. after 7 days	1034	3
Wt. after 11 days	1040	1.5
Wt after 16 days	1047	1.4
Wt. after 19 days	1050	1
Wt. after 27 days	1056	0.75
Wt. after 41 days	1064	0.57
Wt. after 90 days	1074	0.2

The total moisture content of the grains of corn after exposure to a moist atmosphere for 90 days was found to be 19.67 per cent, as determined by drying the ground corn in a Freas oven at 100° C. in air.

From the foregoing table it will be seen that there was a gradual absorption of moisture during the 90 days, but that the rate of absorption was much more rapid during the first week than during the remainder of the time, nearly half of the total increase in weight having taken place in this period. In the first 16 days the increase in weight was 4.7 per cent, while in the remaining 74 days it was only 2.7 per cent. The absorption of water however, seems to have been greater than the apparent gain in weight.

By the end of the 16th day, molds had developed. They increased rapidly and the corn soon acquired a musty odor. At first the growth occurred only on the germs of the grains of corn, but later other molds developed on the starchy and glutinous part. At the conclusion of this experiment the corn was in a badly damaged or spoiled condition.

ACIDITY—The following acidity determinations were made on this spoiled corn and also on sound grains of corn to show by comparison what changes had taken place in the acidity of the grains as a whole and in some of its separate parts, during the experiment.

TABLE II—ACIDITY OF SPOILED AND SOUND CORN GRAINS, EXPRESSED AS CC. OF NORMAL NaOH PER KILO

	Spoiled corn Cc.	Sound corn Cc.
Whole grains	57.6	18.0
Degermed grains	20.8	17.6
Germs only	336.0	52.0

From Table II it will be seen that the acidity of the entire grain had increased more than 3 times while, in the degermed portion of the grain, the increase was slight. The acidity in the germs had increased more than 6 times, showing that the germ is the seat of the greater part of the acidity of the grains of spoiled corn.

A quantity of the spoiled grains of corn was dried and ground and the fat removed with ether, the excess of ether distilled off and the last traces removed by heating in an atmosphere of natural gas. The oil thus obtained had a dark red color and a musty odor. The acidity was found to be equivalent to 1,450 cc. of normal alkali per kg. of oil. The oil obtained by extracting meal made from the sound corn had a pleasant odor, a light lemon color and an acidity of 56.8 cc. of normal alkali per kg. Qualitative tests showed that all of the sugars and, apparently, the greater part of the starch had disappeared from the germs, as a result of the spoiling.

From the results obtained in this experiment it is to be noted that air-dry corn absorbs moisture readily when exposed to moist air and that when the moisture content of the corn reaches about 15 per cent and the temperature is favorable, molds develop, free fatty acids are liberated, and the sugars and starches in the germ disappear. It is therefore assumed that the results obtained in this experiment indicate the nature of the changes that take place when much larger quantities of corn are spoiled, coincidentally with the growth of molds.

FERMENTATION—In addition to the changes that are brought about in corn by the growth of molds, perhaps even greater and more rapid factors in the deterioration and spoiling of corn are those accompanied by heating, souring, and fermentation. To determine approximately the percentage of moisture necessary to bring about fermentation processes in grains of corn, enough distilled water was added to three 1000-g. samples of corn to make a total moisture content of 15, 20, and 25 per cent, respectively. The jars containing the corn were sealed and kept at an average room temperature of 25° C. They were kept under daily observation and at the end of 10 days each jar was opened and examined more carefully to note any evidence of deterioration. In the portions with 20 and 25 per cent of moisture, some gas pressure had developed and the corn evolved a slight sourish odor, indicating that fermentation was under way. In the sample containing only 15 per cent of moisture no pressure or sour odor were detected, but after standing for another period of 10 days the presence of molds was observed. The growth of molds continued with the prolongation of the experiment but no evidence of fermentation changes was observed at any time during the experiment, which indicates that molds will thrive on corn that contains no more than 15 per cent of moisture, whereas it requires a greater percentage of moisture to bring about fermentation.

After 30 days the acidity of the samples containing 15, 20, and 25 per cent of moisture was found to be equivalent to 23, 30, and 50 cc., respectively, of normal alkali per kg. After 60 days each of the experiments may have been described as follows:

15 per cent of moisture—molds present, musty odor.

20 per cent of moisture—badly damaged, sour odor, grains brownish.

25 per cent of moisture—badly damaged, sour odor, grains dark brown.

A duplicate of the experiment containing 20 per cent of moisture was arranged in a 2-liter, wide-mouthed glass bottle carrying a perforated rubber stopper. The bottle was connected by means of glass and rubber tubing with a gas wash-bottle containing a saturated solution of barium hydroxide. The experiment was allowed to stand undisturbed for several weeks, during which time a considerable precipitate of barium carbonate was formed in the wash-bottle. Upon opening the bottle containing the corn, a sour odor was detected. A portion of the corn was removed, ground, and subjected to steam distillation with water slightly acidified with sulfuric acid. After 300 cc. of distillate had been collected the distillation was stopped. The acid distillate was neutralized with an excess of calcium carbonate and evaporated to dryness. The residue was taken up in hot water and the excess of carbonate filtered out. The filtrate and washings were evaporated to a small volume, and alcohol and strong sulfuric acid added. The pronounced odor of ethyl acetate proved that acetic acid was one of the products of the fermentation.

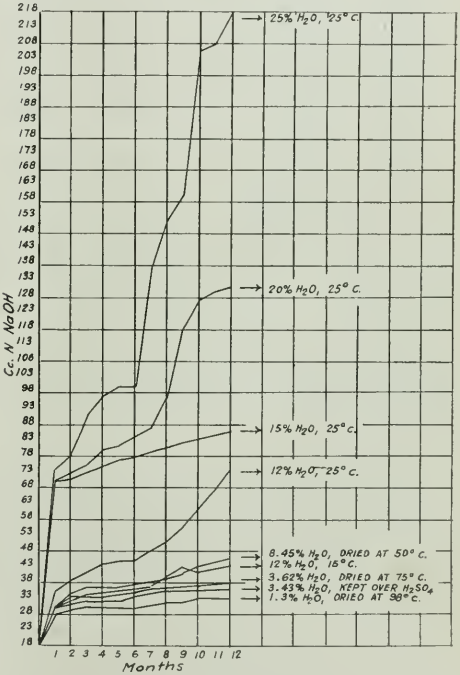
A quantity of the germs was separated from the soured grains of corn, dried, and ground fine. The fat was removed with ether and the dry, fat-free, germ meal was found to contain no sugars and little starch. Apparently the greater part of the starch had undergone fermentation, indicating that in the souring of corn the sugars and starches contained in the germ undergo acetic acid fermentation. It is assumed that the greater part of the odor evolved by souring corn is due to the presence of this acid.

From the foregoing experiments it appears that corn containing as much as 15 per cent of moisture will mold if confined in air-tight vessels at ordinary temperature, whereas, if it contains 20 per cent of moisture or more, it undergoes alcoholic and acetic acid fermentations. It is also shown that sound corn containing 12 per cent of moisture can be kept in good condition in storage for at least 12 months, provided it is not exposed to conditions in which moisture can be absorbed. The chief cause of the deterioration and spoiling of corn appears to be that it has never been dried to a moisture content safe for storage in large quantity or, if it has been so dried, moisture has been absorbed. Corn that has been dried to a moisture content of 12 per cent may be exposed during slow processes of loading or unloading, or during transportation in cars which are not closed sufficiently tight to exclude moist air, until enough moisture is absorbed to make it unsafe for storage. Apparently the reabsorption of moisture is a very important cause of the spoiling of large quantities of export corn while in transit to European ports. If corn containing no more than 12 per cent of moisture were stored in perfectly dry holds and so protected that moisture could not enter, there appears to be no reason why such corn should not keep in a sound condition during transportation on the ocean.

CORN MEAL

What has been said in regard to corn applies in a general way to corn meal. There is, however, one very important deterioration that takes place in corn meal which does not occur in unbroken grains of corn. It has been stated in the discussion that sound grains of corn containing no more than 12 per cent of moisture could be kept without any appreciable alteration for long periods of time. It is well known that this is not the case with corn meal.

In a series of experiments to determine the cause of the deterioration of corn meal, eleven 1000-g. samples of fresh meal made from one of the parts into which the original large sample of grain corn was divided, were sealed in glass jars.



At the first of each of the 12 months through which the experiments were carried on, 25 g. of meal were weighed from each of the 11 jars for acidity determinations, which were made as follows: Each 25-g. portion of meal was transferred to a clean, dry 250-cc. glass bottle and treated with 100 cc. of neutral, 80 per cent alcohol. The bottles were closed with clean rubber stoppers and allowed to stand for 20 hrs. with occasional shaking by hand during this time. This method gave identical results with samples shaken continuously in a shaking apparatus for 6 hrs. At the expiration of the time interval the contents of the bottles were filtered on dry, folded filters.

TABLE III—ACIDITY DEVELOPED IN MEALS OF DIFFERENT WATER-CONTENT, UPON KEEPING IN TIGHT VESSELS[1]

NUMBER OF EXPERIMENT	1	2	3	4	5	6	7	8	9	10	11
INITIAL PER CENT H_2O	12	12	12	12	12	8.46	3.62	1.3	15	20	25
CONDITIONS	Room temp.	15° C.	Oxygen	CO_2	Over H_2SO_4	Dried 50° C.	Dried 75° C.	Dried 98° C.	..	..	..
Aug. 1, 1918	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0
Sept. 2, 1918	34.4	30.4	39 2	37.6	30.4	30.4	30.0	28.0	70.0	70.4	74.0
Oct. 1, 1918	38.8	32.0	39.6	38.0	31.2	34.0	33.2	29.6	71.2	72.4	77.6
Nov. 1, 1918	41.6	34.0	45.2	44.0	32.0	36.8	34.40	30.4	73.6	76.0	90.4
Dec. 2, 1918	44.0	35.2	46.4	44.0	32.0	36.8	34.40	30.4	74.4	80.0	97.6
Jan. 2, 1919	44.8	35.2	46.4	44.8	32.0	36.80	34.40	30.4	76.8	81.6	99.2
Feb. 1, 1919	44.8	35.2	46.4	44.8	33.6	37.6	34.40	30.4	77.6	84.0	99.2
Mar. 1, 1919	48.0	36.8	48.0	48.0	34.4	38.40	35.2	31.20	78.40	87.0	137.6
Apr. 1, 1919	51.2	40.0	54.4	52.8	35.2	39.2	35.2	32.0	80.0	96.0	152.8
May 1, 1919	56.0	41.6	59.2	55.2	35.2	41.6	36.8	32.1	82.4	118.4	160.0
June 2, 1919	62.4	42.0	64.0	60.0	35.2	43.2	37.6	33.6	83.2	126.4	206.4
July 1, 1919	67.2	42.5	67.2	65.6	35.2	44.0	37.6	33.6	84.8	129.6	208.0
Aug. 1, 1919	73.6	43.2	73.6	65.6	35.2	45.6	37.6	33.6	86.4	131.2	219.6
Acidity of oil, cc. normal alkali per kg., August 1919	1377.0	864.0	1530.0	1290.0	386.0	706.0	337.0	180.4	2266.0	664.0	556.0

[1] All at room temperature (25° C.) except 2, at 15° C.

a 50-cc. aliquot part of each clear filtrate was transferred to a 200 cc. Erlenmeyer flask, an equal volume of distilled water and a few drops of phenolphthalein were added, and the solution was titrated to a second degree of pink color with *N*/10 alkali. The results, expressed in terms of cc. of normal alkali per kilo of meal, are given in Table III. They show the degree of acidity attained in each of the different experiments during the time of the investigation. From the data contained in this table, curves have been plotted to show the degree of acidity attained as related to the time, with the exception of Expts. 3 and 4, which show little variation from the results obtained in Expt. 1. In the table are recorded the acidity of the freshly ground meal when it was put into the jars at the beginning of the experiments, on August 1, 1918, and the acidity at the end of each month thereafter. The last line at the bottom of the table shows the acidity of the oil extracted from the meal in each of the experiments a few days after August 1, 1919. Each number represents the number of cc. of normal alkali required to neutralize the acid contained in 1000 g. of meal or oil.

From the table and plot it will be observed that the degree of acidity developed corresponds very closely with the amount of moisture present in each of the experiments. In Expts. 1 to 8, inclusive, it will be noted that the acidity almost doubled during the first month, and thereafter the increase was very gradual. This rapid increase in acidity apparently resulted from the absorption of oxygen which brought about a hydrolysis of the fatty glycerides contained in the oil and the liberation of free fatty acids.

In Expt. 1 the total acidity after 12 months at room temperature was a little more than 4 times the acidity of the freshly ground meal. The increase during the first month was approximately 30 per cent of the total. That the acidity was due to a slow hydrolysis of the fatty glycerides is indicated by the nature of the oil. A steam distillation showed that the meal contained no volatile acids of the acetic series; furthermore, the meal retained a part of its fresh nutty odor throughout the experiment and did not acquire a musty or sour odor.

In Expt. 2 the meal was kept in a refrigerator at 15° C. The retarding effect of the lower temperature upon the development of acidity in the corn meal is shown by comparison with Expt. 1 In addition to a lower acidity in the meal and also in the oil, the meal retained throughout the experiment the odor which is characteristic of meal freshly ground from whole grains of sound corn.

In Expt. 3, in which the meal was kept in an atmosphere of oxygen, the acidity is practically the same as found in Expt. 1, although that of the oil is slightly higher.

In Expt. 4 the meal was kept in an atmosphere of carbon dioxide. The total acidity is not quite as great as in Expts. 1 and 3 and that of the oil is also slightly less.

In Expt. 5 the meal was kept under a bell-jar with a reservoir containing concentrated sulfuric acid. Very little change in the acidity took place in the meal after the first month. After that time the slight increase in acidity is about what would be expected as a result of the loss of moisture that took place from month to month. At the end of the sixth month a moisture determination showed that the meal contained only 3.43 per cent of moisture, so that 8.57 per cent had been absorbed by the acid. The total acidity after 12 months was only 35.2 cc. normal alkali, which was 8 cc. less than in Expt. 2. The acidity of the oil was slightly less than one-half of that of the oil in the same experiment, showing that in the presence of a small amount of moisture there was less hydrolysis of the fatty glycerides at room temperatures than in meal containing 12 per cent of moisture but kept at a considerably lower temperature. In this experiment and also in Expts. 7 and 8 it is clearly demonstrated that as the percentage of moisture in meal decreased the formation of acidity in the meal and also in the oil it contained is correspondingly retarded.

In Expt. 6, 1000 g. of the meal were dried in an electric oven at 50° C., and stirred several times to facilitate a more uniform desiccation. At the end of 72 hrs. the meal was sealed in a jar and a moisture determination showed that it still contained 8.46 per cent of moisture. This drying caused a corresponding retardation of the development of acidity in the meal and oil during the time of the experiment. It also appears that meal containing 8.46 per cent of moisture will develop about the same degree of acidity at room temperature as meal containing 12 per cent of moisture when kept at 15° C.

In Expt. 7 the same quantity of meal was dried in an electric oven for 72 hrs. at 75° C. The meal had browned somewhat as a result of the drying. A moisture determination gave a value of 3.62 per cent. The acidity acquired by the meal and the oil was considerably less than that in the previous experiment and about the same as that in Expt. 5.

In Expt. 8 the meal was dried in a current of dry, natural gas for 24 hrs. at 98° C. The meal acquired a slightly brown color as a result of the drying but was not nearly as dark as the meal that was dried in air at 75° C., indicating that the browning in the latter case was in all probability due to the absorption of oxygen. A moisture determination at 100° C. showed that the meal which had been dried at 98° C. contained 1.3 per cent of moisture. The oil extracted from the meal required only 180.4 cc. of normal alkali per kg. which indicates that in Expts. 5, 6, and 7 the production of acidity in the oil was in some measure accelerated by the process of drying in an atmosphere containing oxygen. The acidity of the oil extracted from freshly ground, sound grains of corn was equivalent to only 63 cc. of normal alkali per kg., which is approximately one-third of the acidity of the oil in Expt. 8, showing that some hydrolysis of the fatty glycerides had taken place as the result of the drying.

In Expts. 9, 10, and 11 enough distilled water was added to each of three 1000-g. samples of meal in porcelain dishes to give a moisture content of approximately 15, 20, and 25 per cent, respectively. After mixing the meal in each dish until the moisture was uniformly distributed, each sample was placed in a glass jar and sealed in the usual way. Determinations on each of the samples, after sufficient time had been allowed for the uniform distribution of moisture through the meal, showed that they contained 15.35, 19.87, and 25.60 per cent of moisture, respectively. Each of the experiments was kept at room temperature and all had undergone considerable deterioration as a result of the addition of the water. At the end of the first month the meal in Expt. 9 had developed molds and a musty odor. The acidity increased more than four-fold in the first month but very slowly during the remainder of the experiment. The acidity of the oil from the meal in this experiment was greater than that found in the oil of any of the other experiments. The meal acquired properties which are characteristic of deteriorations that give rise to musty odors, whereas in Expts. 10 and 11 fermentation changes predominated. In Expt. 10 sour and alcoholic odors were prominent, and in Expt. 11 alcoholic odors were most prominent. It is interesting to note that the oils extracted from the meals in which alcoholic fermentation took place contained much less acid than in Expt. 9. Alcohol, aldehydes, and acetic acid were detected in the distillate from portions of the meal in Expts. 10 and 11 that were subjected to steam distillation.

From the results contained in Table III it is evident that different percentages of moisture in corn meal give rise to different degrees of deterioration. It appears that if the moisture content of corn meal does not exceed approximately 12 per cent only slow hydrolysis of the fatty glycerides takes place and the increase in acidity due to the liberation of fatty acids is gradual. Meal containing this percentage of moisture has been kept in sealed glass jars for 12 months without acquiring any rancid or musty odors. In fact, the meal so kept has even retained some of the sweet odor which is characteristic of fresh meal made from sound, whole grains of corn. The most noteworthy change that took place in the meal during the experiment was the rather rapid increase of acidity which occurred during the first 30 days. At the present time this increase in acidity can only be explained by assuming the presence of a readily oxidizable substance in the germ, which has been protected from the oxygen in the air by the outer integuments surrounding the grain, previous to grinding.

MEAL FROM DEGERMED GRAINS OF CORN

Within recent years millers have received so much complaint about the spoiling of meal made from whole corn that they have been induced to invent machinery for the removal of the germ from corn grains, previous to grinding, hoping thereby to eliminate the chief cause of the spoiling of corn meal.

In Table III the experiments show that meal made from the entire corn grain that does not contain more than 12 per cent of moisture can be kept for a period of 12 months, when air and moisture are excluded, without acquiring any musty or sour odor. The only change observed during this time was a gradual increase in the acidity, which was confined mainly to the oil. How seriously this increase in the acidity of the oil affects the palatableness and wholesomeness of bread made from such meal remains to be determined in future experiments. Except from the standpoint of acidity, the meal is apparently in a perfectly sound condition and has even retained a nutty odor.

From the standpoint of nutrition, meal made from degermed corn is very much inferior to meal made from whole grains of corn, because practically all of a highly nutritious oil, valuable proteins, and a large proportion of the mineral matter are contained in the germ of the corn grain.

The analyses in Table IV show the most important constituents contained in germs and in the degermed grains of corn, expressed as percentages of the moisture-free materials.

TABLE IV

	GERMS	DEGERMED
Crude ash	7.900	0.968
SiO_2	0.057	0.004
Fe_2O_3	0.027	0.003
Mn_3O_4	0.021	0.003
CaO	0.158	0.031
MgO	1.541	0.180
K_2O	2.196	0.156
Na_2O	0.150	0.160
P_2O_5	4.513	0.452
S	0.233	0.137
N	2.634	1.697
Protein (N × 6.25)	16.463	10.606
Fat	28.295	0.196

Inasmuch as the germ constitutes about one-tenth of the whole grain, it follows from these analyses that meal made from degermed grains of corn contains about one-half of the mineral matter present in meal made from the whole grains. Nearly all of the fat is also found in the germ. Since it has been shown that corn oil is one of the most valuable vegetable oils from the standpoint of nutrition, its removal from a food product entails the necessity of substituting some other fat, with the probability that this may often be inferior to the natural oil. It is also well known that bread made from degermed corn meal lacks much of the pleasant nutty flavor imparted to bread made from meal containing the germ. The proteins are also of a much superior quality to an equivalent amount of the proteins contained in the degermed grains of corn. It therefore appears to the writer that the practice of degerming corn intended for human consumption is both harmful and unnecessary and should be prohibited by law.

MOLDS

The different species of molds which developed on certain samples of corn and corn meal have been isolated, grown in pure cultures, and identified.

A dark bluish mold developed on the germs of grains of corn which were exposed to a moist atmosphere for 16 days. Upon growing this species in pure cultures and making a microscopic study of its structure it was identified as *Penicillium expansum*. This mold confined its growth to the germ of the grains of corn and it made the most prolific growth of any of the species that developed on the corn.

Aspergillus glaucus, a species bearing yellow spores, developed in isolated clusters on the germs. Its growth was quite sparce as compared to that of *Penicillium expansum*.

Aspergillus albus, a white mold, developed on the germs of the corn grains after *Penicillium expansum* and *Aspergillus glaucus* had been growing for several weeks.

Citromyces sp., a beautiful white, cottony mold, made a vigorous growth on the degermed, or glutinous and starchy part of the grains of corn. It was not observed growing at any time on the germ of the corn grain.

It is interesting to note that the species of the *Penicillium* and *Aspergillus* appear to attack only the oily portion of the grain. Perhaps this is due in part to the fact that the germ contains more mineral matter as well as more readily digestible proteins, fats, and carbohydrates. Its softer structure perhaps also aids these species in obtaining a foothold more readily. It is quite the opposite in the case of *Citromyces*, and it therefore appears that this mold exercises selective properties towards the medium upon which it develops and grows.

It is not the intention of the writer to infer that these are the only species that will grow on corn or corn meal but simply to state that these are the ones that have developed under the conditions of the experiments described. Doubtless many other species would have developed also had their spores been present.

CONCLUSIONS

1—Excessive moisture is the chief cause of the deterioration and spoiling of corn.

2—Sound grains of corn containing no more than 12 per cent of moisture can be preserved for a considerable length of time.

3—Grains of corn containing 12 per cent of moisture will readily absorb more when exposed to conditions in which free moisture is present.

4—Molds will develop on grains of corn containing as much as 15 per cent of moisture at normal temperatures and with restricted ventilation.

5—Molds cause a very rapid deterioration of the oil, sugar, and starch contained in the germs of corn.

6—Alcoholic and acetic acid fermentations take place when grains of corn containing more than 20 per cent of moisture are deprived of ventilation and kept at normal temperatures.

7—Apparently the cause of export corn spoiling is because it is not thoroughly air-dry (12 per cent moisture) before being put into dry holds and is not kept at that state of dryness during the voyage.

8—The germ contained in sound grains of corn apparently contains an easily oxidizable substance and when fresh meal is made from whole grains of corn and exposed to the atmosphere the acidity increases as a result of the absorption of oxygen from the air.

9—Meal made from whole grains of sound corn containing 12 per cent of moisture can be kept in a condition suitable for human consumption from 4 to 6 months, provided moisture and air are excluded.

10—Corn meal deprived of its moisture undergoes little or no change in acidity.

11—Lowering the temperature retards the development of acidity in corn meal.

12—Meal made from degermed grains of corn is inferior to meal made from whole grains of corn.

ACKNOWLEDGMENT

The author wishes to acknowledge his indebtedness to Dr. A. M. Peter, head of the Department of Chemistry, for helpful criticisms in the preparation of the manuscript

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THE RELATIVE AVAILABILITY OF NITRATE NITROGEN AND COMMERCIAL ORGANIC NITROGEN. FIELD AND CYLINDER EXPERIMENTS[1]

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The question of the availability of nitrogenous fertilizers is one of great importance to the farmer. He desires a material that will be sufficiently available to benefit the immediate crop and at the same time he wishes to guard against undue loss of plant food through leaching.

It is a matter of perhaps equal importance to the fertilizer manufacturer, since he wishes to sell the farmer a fertilizer that will give results, and also to use all the available by-products that may be worked into fertilizers.

Since nitrates are readily soluble in water and are assimilated directly by plants, they are considered readily or immediately available materials. Organic nitrogenous materials must undergo decomposition in order that the nitrogen may be converted into ammonia and nitrates, and are therefore considered less readily available than nitrates. If, however, we allow sufficient time for their decomposition, will they not give as good results as the nitrates; that is, does the greater residual effect of the organic matter balance the ready availability of the nitrates? In other words, taking results covering a period of years, is a pound of nitrogen in the form of organic matter as effective as a pound of nitrate introgen?

For more than twenty years the New Jersey Experiment Station has been making a study of the availability of different nitrogenous materials and the results of much of this work have been published. It seems worth while, at this time, however, to summarize briefly certain phases of this work, and to include new material which has not yet been published. In much of this work the comparison was confined to a nitrate and an organic compound, and on this account this discussion will be confined to results obtained with nitrates and organic materials. The work has been carried on by means of field, cylinder, and pot experiments. The pot experiments constitute a minor part and need not be reported here.

CYLINDER EXPERIMENTS—SERIES A

The work that has been carried on in these cylinders was originally outlined under the rather broad heading "Investigations Relative to the Use of Nitrogenous

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[1] Presented before the Fertilizer Division at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 4, 1919.

Fertilizers" and includes other phases of the nitrogen question than the one immediately under discussion. The cylinders have been described elsewhere[1] and need not be further described here. The soil is a loam (Penn Loam) and has a depth in the cylinder of about 8 in. This top soil rests on a sub-soil, the whole having a depth of about 45 in. Lime and mineral fertilizers (acid phosphate and muriate of potash) have been applied regularly and thus, as far as possible, nitrogen is made the limiting factor.

One cylinder receives no nitrogen and thus becomes the check; one receives nitrate of soda at the rate of 320 lbs. per acre, and one receives dried blood equivalent to the nitrate.

A five-year rotation is practiced on these cylinders, and the results are now available from four such rotations, giving a continuous 20-yr. record. The rotation consists of a year of corn, 2 yrs. of oats, one year of wheat, and one of timothy. Fertilizers are applied for each of these main crops. A residual crop of corn follows each oat crop, but no additional fertilizer is applied for the corn.

A careful record is kept of the amount of nitrogen applied to each cylinder and also of the amount of dry matter harvested and the nitrogen removed by the crops. Wheat is harvested at maturity and saved as grain and straw. All other crops are harvested as hay or forage and reported as dry matter. In the accompanying table, grain is included in total dry matter.

The average yield of dry matter and the percentage of nitrogen recovered for the twenty years are summarized by 10-yr. periods in Table I.

TABLE I

	Grams Dry Matter per Cylinder		Per cent Nitrogen Recovered	
TREATMENT	1st 10 yrs.	2nd 10 yrs.	1st 10 yrs.	2nd 10 yrs.
Nitrate of soda...	237	243	60.48	64.35
Dried blood......	207	185	39.90	37.48

The figures for each year may be found with other data in a previous report.[2]

From these figures it will be observed that the nitrate has given larger yields and a higher nitrogen recovery than the blood. The nitrate shows an average nitrogen recovery of 62.4 per cent, while the dried blood shows a recovery of 38.7 per cent. Furthermore, the yield with nitrate is slightly higher for the second 10-yr. period than for the first, while the reverse is true for the dried blood.

Taking the 20-yr. average, the dried blood shows an availability of 62 on a basis of 100 for nitrate. From the standpoint of the yield of dry matter, however, dried blood shows a yield of 81 on the basis of 100 for nitrate.

CYLINDER EXPERIMENTS—SERIES B

It is generally understood that nitrogenous fertilizers may have different effects in different soils. For example, in a heavy clay soil, organic materials would decay more slowly than in a light sandy soil, and there is a possibility that in the light soil, the loss of nitrate nitrogen through leaching might be greater than the loss of organic nitrogen, even when used in equivalent amounts.

In order that a study might be made of the relative availability of nitrogen in the form of nitrate of soda and dried blood in soils varying in mechanical composition, 60 cylinders were arranged in 10 series of 6 cylinders each and prepared for the growing of crops. All cylinders were filled with a uniform sub-soil to within about 10 in. of the top, and the soils to be studied were laid on these to a depth of about 8 in. The first 6 cylinders (Series A) were filled with a loam soil, the second 6 (Series B) were filled with the same soil containing 10 per cent of coarse white sand; the third 6 (Series C) were filled with a loam soil containing 20 per cent of the sand and so on to the tenth series (Series J), which were filled with pure sand (a 60 per cent sand series was not included).

All cylinders receive each year a liberal application of carbonate of lime, acid phosphate, and muriate of potash. Two in each series receive no nitrogen, that is, they are the check cylinders, two receive 10 g. of nitrate of soda and two receive dried blood equivalent to the 10 g. of nitrate.

A crop of barley and a residual crop of buckwheat are grown each year, all the fertilizers, however, being applied to the first crop. The two crops are harvested and samples analyzed for nitrogen without separating grain and straw. Yields are reported as total dry matter. The results of 7 yrs. (1912 to 1918, inclusive) are now available and summarized by averages in Table II. From this summary it will be noted that the yields from the nitrate cylinders are greater than those from the blood cylinders throughout the series until the 100 per cent sand series is reached. Here the lasting qualities of the blood are shown by a yield of 70.2 g. of dry matter as against 56.7 g. for the nitrate. It is of interest to note that the yields with both materials are well maintained up to and including 50 per cent of sand. Especially is this true of the nitrate as shown by the 7-yr. average of 155 g. for cylinder F—50 per cent sand—as against an average of 151 g., for the same period, for the four series having 10, 20, 30, and 40 per cent of sand, respectively. The corresponding figures for the blood are 123.2 g. as the 7-yr. average for the series having 50 per cent sand, and 134.5 g. as an average for the four series having 10, 20, 30, and 40 per cent sand, respectively.

TABLE II—AVERAGE YIELD OF DRY MATTER AND PER CENT NITROGEN RECOVERED ON SOILS VARYING IN MECHANICAL COMPOSITION—1912–1918. CROPS: BARLEY AND BUCKWHEAT

(1) Yield of Dry Matter—Grams per Cylinder

	Loam	Per cent Sand								
TREATMENT	Soil	10	20	30	40	50	70	80	90	100
Nitrate of soda.	149	159	146	152	149	155	137	113	104	57
Dried blood....	142	148	131	132	127	123	112	110	92	70
Check.........	80	89	68	67	65	67	47	43	29	18
(2) Average Per cent Nitrogen Recovered										
Nitrate of soda.	54.8	51.8	57.6	61.2	60.2	61.3	60.4	46.8	50.9	31.8
Dried blood....	43.8	45.2	46.0	48.2	45.5	41.2	46.6	48.8	45.1	39.1

Since the yields were greater with nitrate than with dried blood, even where the soil was 50 per cent coarse sand, it seems evident that the loss of nitrate nitrogen must have been less than the loss of organic nitrogen, though we have been accustomed to think that the reverse is true in soils containing considerable sand.

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[1] J. G. Lipman and A. W. Blair, "Investigations Relative to the Use of Nitrogenous Plant Foods, 1898–1912," New Jersey Agricultural Experiment Station, *Bulletin* **288**.

[2] J. G. Lipman and A. W. Blair, "Twenty Years' Work on the Availability of Nitrate of Soda, Ammonium Sulfate, Dried Blood and Farm Manures," Table I, *Soil Science* [4], **5**, April 1918.

The average percentage of nitrogen recovered in the crops from the nitrate cylinders is greater than the average from the blood cylinders in 8 out of the 10 series. With 70 per cent sand, the recovery from blood is slightly in excess of the recovery from the nitrate, and with 100 per cent sand, the average stands, nitrate 31.8 per cent and blood 39.1 per cent.

The percentage of nitrogen recovery is well maintained for both nitrate and blood in soil mixtures containing as high as 70 per cent sand. Indeed, where the nitrate was used, the recoveries are higher with 30, 40, 50, and 70 per cent sand than with 10 and 20 per cent sand. Where blood was used, the highest average recovery was with 80 per cent sand and the next highest with 30 per cent sand. The average recovery for all nitrate cylinders is 8.7 per cent higher than the average for all blood cylinders.

FIELD EXPERIMENTS—NITRATE OF SODA AND NITRATE OF LIME COMPARED WITH DRIED BLOOD, FISH, AND TANKAGE

In a study of so important a problem, it did not seem wise to rely entirely on cylinder experiments for data, and therefore, in 1908, 40 one-twentieth acre field plots were laid out for use in a detailed study of the relative availability of a number of nitrogenous materials. Since calcium nitrate was claiming attention as a fertilizer at this time, it was included among the other materials. The figures reported herewith in Table III are the averages of 10 yrs. results from the sodium and calcium nitrate plots on the one hand, and the dried blood, fish, and tankage (organic nitrogen) plots on the other.

TABLE III—AVERAGE YIELD OF DRY MATTER AND PER CENT NITROGEN RECOVERED—FIELD EXPERIMENTS 1908-1917

	Average Lbs. Dry Matter Per Acre		Per Cent Nitrogen Recovered	
TREATMENT	First 5 yrs.	Second 5 yrs.	First 5 yrs.	Second 5 yrs.
Nitrate nitrogen, no lime	4191	3432	38.2	31.8
Nitrate nitrogen with lime	4467	3462	51.0	28.8
Organic nitrogen, no lime	3821	2856	27.3	25.4
Organic nitrogen with lime	3734	3063	28.5	24.9

A 5-yr. rotation has been followed, the crops being for the first 5-yr. period, one year of corn, 2 yrs. of oats, one year of wheat and one year of timothy. For the second 5-yr. period the rotation was slightly changed so that there was only one year of oats and 2 yrs. of timothy. A careful record has been kept of the total dry matter produced and of the amount of nitrogen applied as fertilizers, and of the amount removed by the crops.

It will be noted that the nitrate plots gave the largest yield of dry matter and the highest recovery in both periods.

If an average is taken of the yields of dry matter from the limed and unlimed nitrate plots and the limed and unlimed organic fertilizer plots, it is found that the difference is close to 500 lbs. annually in favor of the nitrate plots for each of the two 5-yr. periods. The average nitrogen recovery of all the nitrate plots for the 10 yrs. is 37.4 per cent as compared with 26.5 per cent for the organic fertilizer plots.

The reason for the greater effectiveness of nitrate nitrogen than organic nitrogen is not entirely clear but the residual crop which is grown every year in cylinder experiments (Series B) seems to throw some light on this question. This crop gets practically no benefit from the nitrate—the first crop having utilized practically all that was not lost in some way—whereas it is benefited slightly by the dried blood. In other words, the organic nitrogen does have a slight residual effect, whereas the nitrate has practically no residual effect. However, the initial effect of the nitrate so much exceeds the initial effect of the organic nitrogen that the total recovery is distinctly in favor of the nitrate. It would appear, therefore, that the nitrate is especially beneficial to the plant in the early stages of its growth at a time when the organic material has not yet become fully effective, and having thus obtained a good start, the plant grows rapidly and utilizes the nitrogen to such good advantage that the loss is really less than from a material that is not so readily soluble. Furthermore, the good start which the nitrate gives the plant enables it to utilize the soil moisture and mineral plant food to better advantage than the plant which is slower in getting started.

The writer wishes to give due credit to the late Dr. E. B. Voorhees, and to Dr. Jacob G. Lipman for their part in planning, inaugurating, and conducting for some time the experiments here described.

THE DETERMINATION OF CELLULOSE IN WOODS

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Received July 19, 1919

In a previous paper[1] the author proposed a tentative scheme for the proximate analysis of woods, the object of which was to account for practically all of the constituents present. It was then shown that the process was fairly successful with the coniferous woods but not with the hardwoods.

It was recommended that the dried sample be extracted successively with benzene and alcohol, then digested successively with water and one per cent sodium hydroxide solution and the amounts of material removed by each of these reagents recorded as analytical data. It was assumed that the resulting residue represented a purified lignocellulose suitable for both the cellulose and lignin determination. The hydrolytic treatments with water and the dilute alkali were considered as resulting in the removal of the less resistant lignins and cellulose corresponding approximately to the "proto" and "hemi" bodies of König's classification,[2] leaving the "ortho" forms, of true cellulose and lignin, practically unattacked.

The former paper offered data based upon separations made by this alkaline treatment, with a full realization of the arbitrary character and doubtful propriety of the procedure. It was believed, however, that some form of hydrolysis was necessary to secure a cellulose free from hemicelluloses. The various suggested processes were carefully considered. While there was a lack of comparative data as to results by these methods, theoretical considerations seemed to indicate moderate alkaline hydrolysis as least objectionable and it was accordingly tentatively adopted.

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[1] THIS JOURNAL, **11** (1919), 556.

[2] *Z. Nahr. Genussm.*, **28** (1914), 177.

Results of investigations of the effects of acid and alkaline hydrolysis upon wood cellulose, here presented, indicate a revision of some of the methods and opinions of the earlier paper.

The original method of Cross and Bevan for the determination of cellulose[1] directed that the material should be treated with a one per cent sodium hydroxide solution previous to chlorination and that sodium hydroxide should be added to the sulfite solution used in dissolving the chlorinated product. The addition of alkali previous to chlorination was practiced, partly because it was considered essential to the removal of hemicelluloses that would otherwise contaminate the final product and partly to assist in removing the lignin and opening up the tissues for attack by the chlorine.

A critical study of this and other cellulose processes published by Renker[2] in 1910 showed that the use of alkali either before or after chlorination is not essential to obtaining a residue free from lignin, but that if the alkali is used a lower percentage residue is obtained. He accordingly concluded that the cellulose is attacked by alkaline treatment and modified the process to omit it. The data offered by various authors, while not strictly comparable, indicate that the highest results for cellulose are obtained by the Renker method in which neither acid nor alkaline preliminary treatment is used.

Renker's findings were confirmed by Schorger,[3] of the United States Forest Products Laboratory, who used the Renker modified method in his investigations of American woods.

Schorger found that when digestion in one per cent sodium hydroxide was practiced there was a considerable decrease in the percentage of cellulose in the hardwoods. The difference was less marked in the conifers.

Johnsen and Hovey[4] have proposed a process of acid hydrolysis, using a mixture of acetic acid and glycerin previous to chlorination, claiming that this produces a purer cellulose, and that the lower figures resulting represent a closer approach to the true cellulose value than Schorger's results by the Renker method. They obtained results which were consistently lower by 2 to 4 per cent than those obtained when no hydrolytic treatment was used.

It is obvious that the three methods proposed, *i. e.*, no preliminary hydrolysis, alkaline hydrolysis with one per cent sodium hydroxide, and acid hydrolysis with acetic acid and glycerin, are not comparable upon the basis of cellulose yield alone. A smaller yield may indicate a purer cellulose and accordingly a more accurate determination, or it may indicate a partial destruction of the cellulose itself and a less accurate result. It is necessary to determine the purity of the products in order to compare the merits of the processes. The data on this point are somewhat meager. It appears that with suitable mechanical preparation of the material all of these processes are capable of yielding material free from lignin. The residue by Renker's method gives a considerable yield of furfural on distillation with hydrochloric acid and for that reason the method has been criticized as yielding an impure cellulose. The claims of Johnsen and Hovey for the superiority of their process are based partly upon the reduced furfural yield of the residue. It is to be noted in this connection that the process of alkaline hydrolysis has had for one of its objects the removal of xylan, or wood gum, a furfural-yielding substance. The available data indicate that the residues by all of these cellulose processes contain some furfural-yielding material resistant to the hydrolytic treatments employed.

Cross and Bevan[1] have maintained that this highly resistant furfural-yielding material is not a pentosan but an oxycellulose and a normal constituent of celluloses derived from lignified tissues. These views have been disputed by König[2] but have been accepted by most cellulose investigators.

From the above discussion it is clear that we are much in need of a standard of purity and a more exact definition of cellulose. As applied to the cellulose of woods, the term has been commonly accepted as a group designation, signifying a residue remaining after successive alternate treatments with chlorine and dilute sodium sulfite solution until free from lignin derivatives. The amount and character of the residue necessarily varies considerably with the treatment it has undergone preliminary to chlorination.

Cellulose derived from cotton is a homogeneous substance with such definite chemical properties that it is quite generally accepted as a chemical entity. It is much more precisely described as "normal cellulose" and is characterized by the absence of free carbonyl, methoxy, or furfural-yielding groups. It has been quantitatively hydrolyzed to dextrose and has accordingly been described as a "polydextrose anhydride."[3]

Cellulose residues derived from woods show no such homogeneity. Cross and Bevan[4] have shown that the celluloses derived from lignified tissues are mixtures of a cellulose similar to or identical with the normal cellulose of cotton. and other celluloses of less stability which are distinguished from normal cellulose by a feebler resistance to reagents and by the presence of methoxy and furfural-yielding groups.

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[1] "Cellulose," 2nd Ed., p. 95.

[2] "Bestimmungsmethoden der Cellulose."

[3] THIS JOURNAL, **9** (1917), 556 and 561.

[4] *Paper* [23], **21** (1918), 36, also *J. Soc Chem. Ind.*, **37** (1918), 132–7T.

[1] "Cellulose," 2nd ed., pp. 82, 101.

[2] "Bestimmung der Zellulose in Holzarten und Gespinstfasern."

[3] "Researches on Cellulose," III, p 42.

[4] "Cellulose," 2nd Ed., p. 93.

A partial measure of the industrial importance of a wood cellulose is the amount of normal cellulose present. In manufacturing wood pulp by the sulfite and soda processes all except the normal form is largely destroyed. Celluloses derived from woods have found but little application in the nitrocellulose and other cellulose ester industries, chiefly because the presence of other celluloses than the normal results in byproducts of low stability and diminished yields of main product. These points have been recently covered in a paper by Baker.[1]

In experimental research, at least, a statement of the analysis of woods and other fibrous products might well include not only the total amount of cellulose obtained by chlorination, but also the amount of normal cellulose contained in this residue. In the present investigation the determination of the normal cellulose in the residues is used to indicate the extent to which the cellulose has been attacked by the preliminary hydrolysis. A diminished yield of normal cellulose indicates that the treatment has been too severe and has attacked the most resistant member of the series.

As a means of determining the normal cellulose, the mercerization test of Cross and Bevan[2] is available. It depends upon the fact that normal cellulose unites with sodium hydroxide of mercerizing strength to form alkali cellulose and is regenerated without loss of weight upon diluting and washing out the lye. As the other celluloses are dissolved by this treatment, the residue may be dried and weighed as normal or α-cellulose. The sodium hydroxide solution upon neutralization with acetic acid yields part of the dissolved cellulose as a precipitate, while a third portion of the cellulose remains permanently in solution. These celluloses are designated as β- and γ-cellulose, respectively, and signify progressively less resistant forms of cellulose.

EXPERIMENTAL

Fine redwood sawdust was obtained by sifting somewhat coarse sawdust through a 50-mesh sieve. The sample was sawed from slabs and accordingly consisted chiefly of sapwood. There was no attempt to make the sample representative of the species as the data were wanted for comparative purposes only. For the same reason the data have not been calculated to a dry basis but refer to material with an average moisture content of 11.62 per cent.

EXTRACTION—Portions of 2 g. each were weighed into alundum thimbles, placed in a Soxhlet apparatus, and extracted with benzene for 6 hrs., then with 95 per cent alcohol for 6 hrs. The residues were experimented upon with the three different treatments here described.

(1) *Renker Modification of Cross and Bevan's Method*—Hydrolytic treatment was entirely omitted. The material was transferred to Gooch crucibles provided with filtering disks of mercerized cotton cloth and washed with hot water.

(2) *Original Cross and Bevan Method*—The material was similarly washed, and transferred to Erlenmeyer flasks provided with reflux condensers. 100 cc. of a one per cent sodium hydroxide solution were added and the material digested for an hour at boiling temperature. At the end of that time it was filtered through Gooch crucibles, washed with hot water, dilute acetic acid, and finally with hot water again.

(3) *Johnsen and Hovey Method*—The material was placed in Erlenmeyer flasks provided with ground-in reflux condensers. To each flask were added 75 cc. of a mixture of glacial acetic acid and glycerin (sp. gr. 1.26) in the ratio of their molecular weights (60 : 92). The mixture was placed in a paraffin bath and heated for 4 hrs. at 135° C. At the end of that period the contents of the flasks were filtered and washed first with strong acetic acid, then dilute acid, and finally with hot water.

The washing with acetic acid of diminishing concentration was intended to prevent reprecipitation within the residue upon dilution. The lack of agreement in the results, as shown in the table below, may be due to this reprecipitation. No quantitative significance should be attached to the loss of weight by this treatment.

Experimental data, showing the loss of material in each treatment, are given in Table I.

TABLE I—LOSS OF WEIGHT BY VARIOUS HYDROLYTIC PROCESSES

Loss on drying	11.62
Loss on extraction with benzene	0.30
Loss on extraction with alcohol	3.88
Material removed by above processes	15.80
Residue by difference	84.20
Residue after washing with water: 4 determinations varying from 84.13 to 84.60 show that no measurable loss of material occurs by this process.	
Residue after digestion in one per cent sodium hydroxide: 4 determinations varying from 76.40 to 77.71, average	76.87
Loss in weight by this process	7.33
Residue after treating with acetic acid and glycerin: 3 determinations varying from 76.12 to 77.62, average	76.76
Loss in weight by this process	7.44

The figures are in all cases the average of several determinations and are expressed in percentages of the air-dry sawdust (11.62 per cent moisture).

CHLORINATION—The residues from all these processes, without any intermediate drying, were submitted to chlorination by the method of Sieber and Walter[1] (also used by Johnsen and Hovey),[2] which was found to be convenient and reliable. A comparison of this method with the vacuum chlorination method recently proposed by the present author,[3] showed that the Sieber and Walter method yields a product as nearly free from lignin and oxycellulose as the former method and is simpler to manipulate. The Sieber and Walter method is without doubt the most convenient process thus far devised and will probably be eventually adopted as the standard cellulose method.

The apparatus used is shown in the accompanying cut. The material was contained in a Gooch crucible supported over a suction filtration flask in the usual manner. Around the filtration tube was fitted an inverted rubber stopper by means of which the crucible was capped with a glass adapter for the introduction of the chlorine. The smaller connecting tube of the adapter was attached to a chlorine apparatus and a moderately rapid stream of washed chlorine was drawn through the material for 20 min. by means of a suction pump. The crucible was then removed and dilute sulfurous acid added to the residue, after which it was washed with hot water. The crucible and its contents were placed in a 50 cc. beaker, sufficient 3 per cent sodium hydroxide solution added to almost cover the material, and the whole heated on the steam bath for three-quarters of an hour. The crucible was then removed from the solution and placed on a suction filter. Sulfite solution was poured through and the residue well washed with hot water.

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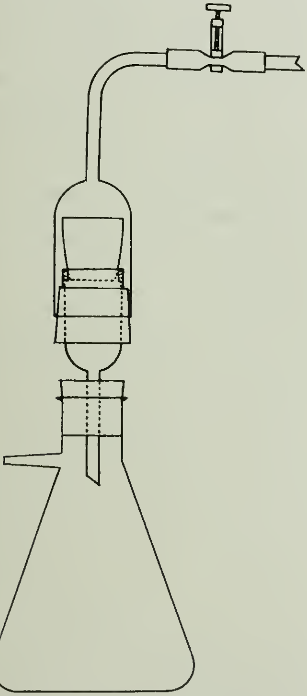
[1] *Paper* [23], **21** (1918), 78.

[2] "Researches on Cellulose," III, p. 22.

[1] *Papier-Fabr.*, **11**, 1179–82; *Chem. Abs.*, **8** (1914), 1202.

[2] *Loc. cit.*

[3] THIS JOURNAL, **11** (1919), 556.



The chlorination and sulfite treatments were then repeated 3 times, the periods of exposure to the gas being 15, 15, and 10 min., respectively. After final sulfite digestion the material was washed thoroughly with hot water, dried for 16 hrs. at 100° C. and weighed as "total cellulose." The crucibles were weighed in weighing bottles having tightly ground glass stoppers.

DETERMINATION OF NORMAL CELLULOSE—The α- or normal cellulose in the total cellulose residues by the three processes was determined by the Cross and Bevan mercerization test.[1] The dry material was transferred as completely as possible to a beaker, 50 cc. of cold 17.5 per cent sodium hydroxide solution added and the whole allowed to stand for half an hour. It was then diluted with 50 cc. of cold water, filtered off on the original Gooch crucible and washed with about one liter of cold water, several times with dilute acetic acid and finally with sufficient cold water to remove all of the acid. It was then dried for 16 hrs. at 100° and weighed as α-cellulose.

Below are given the yields of total cellulose and α-cellulose obtained after the three different preliminary treatments.

TABLE II—COMPARISON OF METHODS OF PRELIMINARY HYDROLYSIS AS APPLIED TO WOODS

Results in percentages of air-dry wood (11.62 per cent moisture)

	TOTAL CELLULOSE		α-CELLULOSE		Ratio α-Cellulose: Total Cellulose
	Individual	Av.	Individual	Av.	
(1) Renker's modification of Cross and Bevan's method. No hydrolysis	47.93		36.04		
	48.46		36.02		
	48.97		36.71		
	48.77		36.84		
	48.91		37.09		
	48.27		36.76		
	48.24	48.51	36.99	36.64	0.75
(2) Original Cross and Bevan method. 1 hr. with 1 per cent sodium hydroxide at boiling temperature	45.86		35.38		
	46.28		35.49		
	45.85		35.25		
	45.07		35.03		
	45.64		35.76		
	46.29	45.83	35.55	35.41	0.77
(3) Johnsen and Hovey method. 4 hrs. with acetic acid and glycerin at 135° C.	44.04		34.60		
	44.11		34.73		
	44.37		34.70		
	44.49	44.25	34.53	34.64	0.78

DETERMINATION OF FURFURAL—Determinations were made of the furfural yield of the total and α-cellulose residues by the various processes. This was done by the usual method of distilling the material with 12 per cent hydrochloric acid and precipitating the distillate with phloroglucin solution. The method as applied to woods is described in detail by Schorger.[1] No distinction between furfural and methyl furfural was made.

TABLE III—FURFURAL YIELD OF PRODUCTS

In percentages of air-dried material (11.62 per cent moisture)

	FROM TOTAL CELLULOSE		FROM α-CELLULOSE	
	Individual	Av.	Individual	Av.
(1) Renker's process. No hydrolysis	2.66		0.52	
	2.36		....	
	2.69		0.48	
	2.38	2.52	0.51	0.50
(2) Cross and Bevan's process. Alkaline hydrolysis	2.67		0.31	
	2.63	2.65	0.24	0.27
(3) Johnsen and Hovey's process. Acid hydrolysis	2.18		0.25	
	2.20	2.19	0.27	0.26

HYDROLYSIS OF COTTON—In order to determine whether the destructive effect of hydrolytic agents upon cellulose is peculiar to cellulose derived from woods, experiments were made with cotton. The material used was a piece of cotton sheeting which had been repeatedly laundered and might therefore be considered a residue consisting of highly resistant cellulose, mostly of the normal type. It was snipped into small pieces, portions weighed out and submitted to various treatments, after which it was chlorinated in the usual way, the residues treated by the mercerization process and the α-cellulose determined.

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[1] "Paper Making," 1916 Ed., p. 97.

[1] THIS JOURNAL, 9 (1917), 556.

TABLE IV—COMPARISON OF METHODS OF PRELIMINARY HYDROLYSIS AS APPLIED TO COTTON

In percentages of air-dried material (4.65 per cent moisture)

TREATMENT	Total Cellulose	α-Cellulose	Ratio α-Cellulose: Total Cellulose
A. No hydrolysis	89.90	85.32	0.95
B. 1 per cent sodium hydroxide 1 hr. boiling	85.33	82.16	0.96
C. Acetic acid and glycerin 4 hrs. at 135° C.	85.91	80.63	0.94
D. 40 per cent acetic acid 4 hrs. boiling	85.52	81.28	0.95
E. 20 per cent acetic acid 4 hrs. boiling	86.44	81.68	0.94

DETERMINATION OF TEMPERATURE EFFECT—To determine whether weak acid and alkaline solutions exerted any appreciable effect in the cold, samples of sawdust were extracted with benzene and alcohol as before, allowed to stand in such solutions for 5 days, then filtered, washed, dried and weighed, chlorinated as usual, and again dried and weighed.

TABLE V—EFFECT OF COLD DILUTE ACID AND ALKALI UPON WOOD

Results in percentages of air-dried material (11.62 per cent moisture)

TREATMENT	Residue after Treatment	Total Cellulose
5 days in cold, 1 per cent sodium hydroxide	81.37	48.45
5 days in cold, 5 per cent sodium hydroxide	80.50	47.65
5 days in cold, 1 per cent hydrochloric acid	83.11	48.08
5 days in cold, 5 per cent hydrochloric acid	82.54	48.89

A comparison of Table V with Table II shows that the magnitude and the variation of the cellulose values in these last tests is practically identical with those in tests where all treatment is omitted. We may therefore conclude that these reagents are wholly without effect in the cold.

An attempt was made to obtain some information as to the composition of the less resistant portion of the cellulose residue. Several portions of total cellulose prepared by the Renker method were submitted to mercerization, the solutions containing the other celluloses were neutralized, and the precipitated β-celluloses, after standing on the steam bath for some hours to coagulate, were filtered off on gooches, washed, dried and weighed. The filtrates were hydrolyzed by adding hydrochloric acid and boiling under a reflux condenser for 3 hrs., and the reducing sugar determined by Allihn's method. The results were variable and unsatisfactory. It is well known that on heating with dilute acids the hexose carbohydrates decompose more or less to levulinic and formic acids. It is believed that much of the less stable cellulose material was lost through this reaction and through conversion into furfural.

DISCUSSION

It is obvious that all methods involving hydrolysis result in a reduced yield of both total and α-cellulose. The ratios of the substances are practically identical in the various processes, indicating that they are destroyed in the same proportion. This shows that the hydrolytic processes do not accomplish the purpose for which they were designed; that is, instead of exercising a selective action and producing a purer cellulose, the reagents apparently attack all of the resistant carbohydrates with equal vigor. It appears, therefore, that the use of preliminary hydrolytic treatments is inadmissible in an accurate cellulose process. Renker's method is to be regarded as the most suitable process since it gives a product as pure as the others and in maximum yield.

The experiments with cotton show that celluloses of this type are equally susceptible to hydrolytic action. The behavior of wood celluloses under the action of hydrolytic agents is therefore not to be ascribed to any peculiarities of constitution or to the fact that it is derived from lignified material. Apparently celluloses from any source are readily attacked by weak acid or alkaline solutions at boiling temperatures but are unaffected by similar reagents in the cold.

The furfural yield of normal cellulose is in every case insignificant. The total celluloses give furfural yields that do not differ materially from each other and it may be concluded that the hydrolytic processes do not remove any appreciable amount of the furfural-yielding complexes from the product. Untreated wood yields 5.84 per cent of furfural (average of two determinations). About half of the furfural-yielding substances, therefore, disappear during chlorination. The missing portion is probably all to be found in the chlorination filtrates and washings and no doubt represents that present as xylan or wood gum. The furfural still remaining in the residue and resistant to hydrolysis probably originates not in pentosans but in oxycellulose.

The total cellulose residue obtained by the Renker process was tested for mannan and galactan with negative results. The original wood (redwood), however, has been found by the author to contain 2.48 per cent of mannan and 0.47 per cent of galactan. The hemicelluloses therefore disappear during chlorination. The filtrates and washings incidental to the chlorination operations contain considerable amounts of reducing sugars which are no doubt the hydrolyzed products of the hemicelluloses. It is therefore evident that the chlorination process itself involves sufficient hydrolysis to remove the hemicelluloses and that no additional hydrolytic treatment is necessary.

Hägglund[1] has shown that sulfite waste liquor contains xylose, mannose, galactose, and levulose, but no dextrose. On the other hand, when wood was hydrolyzed with dilute sulfuric acid (0.5 per cent) he obtained dextrose, in solution as well. The researches of Ost and Wilkening[2] have shown that normal cotton cellulose may be practically quantitatively hydrolyzed to dextrose, and presumably the same is true of the α-cellulose of woods. Since the β-cellulose of woods is largely hydrolyzed by the sulfite process[3] and since the sulfite liquor contains no dextrose, it is evident that the β-cellulose does not hydrolyze to dextrose. Possibly β-cellulose is the source of the levulose found in sulfite liquor. There seems to be no direct experimental evidence on this point.

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[1] *Biochem. Z.*, **70** (1915), 416.

[2] *Chem.-Ztg.*, **34** (1910), 461.

[3] Cross & Bevan, "Cellulose," 2nd Ed., p. 98.

At present there prevails a rather uncertain conception of the significance of the term "cellulose" as applied to material derived from woods. In general, it may be understood to mean a product prepared by processes of sufficient intensity to remove all extractives (resins, dyes, etc.), incrusting substances (lignin), and hemicelluloses (condensed carbohydrates of pentose, mannose, and galactose basis) and limited in their action to those bodies. The chlorination process as applied to wood material, treated with non-hydrolyzing solvents only, fulfills these requirements. The definition of cellulose as a residue remaining after alternating treatments with chlorine and sodium sulfite solution may be accepted if we add the limitation that the process be preceded with non-hydrolyzing treatments only.

The residue so obtained should be free of lignin and hemicellulose, including pentosans, mannans, and galactans. It may contain α-, β-, and γ-celluloses corresponding to the definitions of these bodies implied by the conditions of the mercerization test, also furfural-yielding complexes, but should be free from easily hydrolyzable pentosans.

SUMMARY

I—A comparison is made of three proposed methods of treating woods and other lignified materials previous to chlorination in the cellulose determination. These methods consist of (1) absence of hydrolysis, (2) alkaline hydrolysis, and (3) acid hydrolysis, restricted in each case to the degree of intensity considered necessary for avoiding attack upon the cellulose proper.

II—The data show that all processes involving preliminary hydrolysis result in diminished yield of α-cellulose as well as total cellulose, and are therefore unacceptable as accurate cellulose processes.

III—The ratios of α-cellulose to total cellulose are practically the same whether or not preliminary hydrolysis is used. This shows that the highest type of cellulose is as strongly attacked during hydrolysis as the lower types.

IV—During the treatments incidental to chlorination the hemicelluloses are hydrolyzed and dissolved in the filtrates and washings. Preliminary treatment with the object of removing the hemicelluloses is therefore superfluous.

V—A considerable proportion of the furfural-yielding complex (probably oxycellulose) remains in the residue practically unaffected by any of the hydrolytic treatments employed. The rest of the furfural-yielding material (probably xylan) is readily hydrolyzed and dissolved during chlorination.

VI—The significance of the term "cellulose" as applied to wood products is discussed.

A RAPID ACCURATE METHOD FOR THE ANALYSIS OF AN IRON ORE

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Received September 22, 1919

The relative merits of the dichromate and permanganate methods for the analysis of an iron ore are too well known to warrant any lengthy discussion of them here. It is advisable, however, to recall those particular points which have a special bearing on this article.

ARGUMENTS FOR AND AGAINST PERMANGANATE AS A STANDARD OXIDIZING AGENT

The permanganate method is generally used to-day, due to the fact that permanganate acts as its own indicator and gives an easily obtainable end-point. Many possible errors, however, must be guarded against. The instability of the reagent makes necessary quite frequent restandardization. The solution should be kept in colored bottles and out of the light as much as possible. The introduction of organic matter, even dust, causes a reduction to manganese dioxide. Treadwell, after giving data showing that the permanency of potassium permanganate is greatly increased by heating the solution, or allowing it to age for 2 wks., and then filtering through asbestos, concludes by saying,[1] "For very accurate work, however, it is advisable to restandardize the solution frequently."

Another troublesome feature is the reducing action of the chloride ion on the permanganate ion, necessitating the use of the rather unsatisfactory preventive solution with its possibly useless components.[2] Fuming sulfuric acid may, of course, be substituted, but this operation, even in the hands of an experienced analyst, is liable to introduce a percentage of error which is almost prohibitive in quantitative work.

DISCUSSION OF THE USE OF POTASSIUM DICHROMATE AS A STANDARD OXIDIZING AGENT

The dichromate solution, on the other hand, is a permanent standard, little affected by traces of organic matter. The dichromate ion is, moreover, not reduced by the chloride ion, thus making the use of preventive solution, or its unsatisfactory substitutes, unnecessary. The necessity of using ferricyanide as an outside indicator with dichromate, however, causes most analysts to prefer the permanganate titration.

Speaking of the use of dichromate as a standard oxidizing agent, Foulk says:[3] "A solution of potassium dichromate, through a strong oxidizing agent, is perfectly stable under ordinary laboratory conditions. It is unaffected by light, is not acted upon rapidly by organic matter, and does not act on dilute hydrochloric acid. The salt ($K_2Cr_2O_7$) is easily obtained pure, and, if recrystallized and dried, is one of the best standard substances to be used in determining the exact strength of oxidizing and reducing solutions." He adds further: "The chief objection to be made to standard solutions of potassium dichromate is the fact that no convenient indicator has yet been found for it."

The writers realized, therefore, that if the dichromate method could be used with an accurate indicator in the solution, it would be by far the preferable method. Little and Fenner have shown in their "Modified Dichromate Method for the Analysis of Glycerin,"[4] that after oxidizing glycerin with a measured amount of potassium dichromate, the excess of dichromate can be determined by adding potassium iodide and titrating with thiosulfate, using starch as an indicator. In this way the use of an outside indicator as directed in the Official Dichromate Method[1] for glycerin analysis was eliminated.

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[1] Treadwell and Hall, "Analytical Chemistry," p. 561.

[2] Hough, *J. Am. Chem. Soc.*, **32** (1910), 539.

[3] "Quantitative Analysis," p. 167.

[4] *J. Am. Leather Chem. Assoc.*, June 1917.

THEORETICAL DISCUSSION

It will be seen at once that the same scheme could be used in a ferrous iron titration were it not for the presence of the ferric ion in solution, which is reduced by the iodide ion and iodine liberated. The question then is how this interference of the ferric ion can be eliminated. To answer this question, let us study the reversible oxidation and reduction reaction $2Fe^{+++} + 2I^- \rightleftarrows 2Fe^{++} + I_2$, and consider it in terms of the two separate reactions:

$$(A)\quad 2Fe^{+++} \rightleftarrows 2Fe^{++} + (2+)$$

$$(B)\quad 2I^- + (2+) \rightleftarrows I_2$$

The tendency of Equation A in acid solution for ordinary concentrations is in the direction of the formation of ferrous ions. Like all similar reactions, however, equilibrium can be established by a proper adjustment of the two concentrations, and Peters has furnished data[2] which show that the reaction is in equilibrium when the following relative concentrations exist:

$$\frac{CFe^{++}}{CFe^{+++}} = 10^{17} \text{ at } 25^\circ \text{ C.}$$

Similarly, the action in Equation B is, for ordinary concentrations, in the direction of the formation of iodide ion, and Küster and Crotogino have shown[3] that at equilibrium the relative concentrations of the two components are approximately as follows:

$$\frac{(CI^-)^2}{CI_2} = 5.6 \times 10^{29} \text{ at } 25^\circ \text{ C.}$$

Making use of these two constants and applying them to the reversible equation

$$2Fe^{+++} + 2I^- \rightleftarrows 2Fe^{++} + I_2$$

we have at equilibrium,[4]

$$\frac{(CFe^{+++})^2 \times (CI^-)^2}{(CFe^{++})^2 \times CI_2} = K = \frac{5.6 \times 10^{29}}{(10^{17})^2} = 5.6 \times 10^{-5}.$$

This equation is derived as follows: The quantitative expression of the oxidizing potential of Fe^{+++} is

$$E_1 = \frac{RT}{2} \log \frac{(CFe^{+++})^2}{(CFe^{++})^2} \times 10^{34}.$$

The potential of I° as an oxidizing agent is

$$E_2 = \frac{RT}{2} \log \frac{CI_2}{(CI^-)^2} \times 5.6 \times 10^{29}$$

(assuming 5.6×10^{29} to be correct).

At equilibrium the two potentials will be equal,

$$E_1 = E_2$$

$$\frac{RT}{2} \log \frac{(CFe^{+++})^2}{(CFe^{++})^2} \times 10^{34} = \frac{RT}{2} \log \frac{CI_2}{(CI^-)^2} \times 5.6 \times 10^{29}$$

or $$\frac{(CFe^{+++})^2 \times (CI^-)^2}{(CFe^{++})^2 \times CI_2} = \frac{5.6 \times 10^{29}}{10^{34}} \text{ or } 5.6 \times 10^{-5}.$$

The constant of equilibrium is very small, hence the numerator of the above fraction must be small and the denominator relatively large. This is in accord with the well-known fact that I^- will reduce Fe^{+++} to Fe^{++}. In view of the above expression of equilibrium, it is evident that the oxidation of the iodide ion could most easily be prevented by greatly reducing the concentration of the ferric ion. If this concentration is reduced to a minimum, it will necessitate a change in the concentrations of the other three components. These changes will, of course, be in the direction of reëstablishing equilibrium, and since the concentration of ferric ions has been reduced, equilibrium could be brought about by only increasing the concentration of iodide ions. The concentration of iodide ions is increased by having iodine oxidize ferrous ions to ferric ions, the iodine being changed to iodide.

Thus we see that by reducing the concentration of ferric ions the oxidizing potential for the equation

$$Fe^{+++} \rightleftarrows Fe^{++} + (1+),$$

which is represented by the quantitative expression

$$E \text{ (volts)} = RT \log \frac{CFe^{+++}}{CFe^{++}} \times 10^{17}$$

where R = gas constant and T = absolute temperature, is reduced below the oxidizing potential for the equation

$$I_2 \rightleftarrows 2I^- + (2+),$$

which is represented by the quantitative expression

$$E = \frac{RT}{2} \log \frac{CI_2}{(CI^-)^2} \times 5.6 \times 10^{29},$$

and consequently we have not

$$2Fe^{+++} + 2I^- \longrightarrow 2Fe^{++} + I_2,$$

but

$$2Fe^{++} + I_2 \longrightarrow 2Fe^{+++} + 2I^-.$$

The interference on the part of the ferric ion is, therefore, eliminated.

APPLICATION OF THEORY

The simplest way to keep the concentration of ferric ion low during the titration is by the addition of the fluoride ion, with which it unites to form a highly un-ionized ferric fluoride complex, probably $FeF_6^{\,-}$. The efficiency of the fluoride ion in this connection is easily shown by putting a few cc. of *N*/10 ferric iron solution in a beaker. Dilute to about 200 cc., add about 3 g. of ammonium fluoride and some potassium iodide. Not enough iodine is formed to give even the slightest blue color with starch solution. The concentration of ferric ion has been reduced to a minimum, and the results predicted in the above theoretical discussion have followed. Mott[1] in his short iodide method for the analysis of a copper ore successfully eliminates Fe^{+++} from solution by changing it to the un-ionized ferric fluoride complex.

Therefore, if during the analysis of an iron ore by the dichromate method about 5 cc. in excess of dichromate are added, ammonium fluoride and potassium iodide introduced into the solution, and the iodine taken up by a "hypo" titration, using starch as an indicator, we have a method which possesses all the advantages of the regular dichromate method without the disadvantage of an outside indicator.

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[1] THIS JOURNAL, **3** (1911), 679.

[2] *Z. phys. Chem.*, **26**, 193.

[3] *Z. anorg. Chem.*, **23**, 88.

[4] Stieglitz, "Theoretical Qualitative Analysis," p. 274.

[1] *The Chemist Analyst*, July 1912.

In a discussion of the sodium thiosulfate titration using starch as an indicator, Talbot says: "It may perhaps be regarded as the most accurate of volumetric processes." Treadwell also speaks of it as "The most sensitive reaction used in analytical chemistry." He adds that if the water in which the salt is dissolved is free from carbon dioxide, "The solution (of 'hypo') can be kept for months without suffering an appreciable change in concentration." He found that a 2 mo. old solution, one cc. of which was equivalent to 0.011672 g. of iodine after standing 8 mo., had an iodine equivalent of 0.011667 g. The thiosulfate solution is also easily standardized against the dichromate solution.

USE OF METHOD WITH MOHR'S SALT SOLUTION

The following data were obtained by titrating 25 cc. portions of a Mohr's salt solution with 0.09590 normal dichromate until the end-point, using $K_3Fe(CN)_6$ as an outside indicator, was reached. Different amounts of potassium dichromate were then added, ammonium fluoride and potassium iodide introduced, and the titration finished with 0.06210 normal "hypo."

The volumes of solution were changed over to a $N/10$ basis, and the relation between the excess potassium dichromate taken and the "hypo" necessary to absorb the iodine liberated is shown in Table I.

TABLE I

Cc. $K_2Cr_2O_7$ $N/10$	Cc. $Na_2S_2O_7$ $N/10$
0.96	0.95
1.92	1.90
2.88	2.80
3.84	3.80
4.80	4.70
5.75	5.70
6.71	6.65
7.67	7.65
8.63	8.60
9.59	9.63

Five different samples of a standard Mohr's salt solution (0.09650 normal) were then titrated with the standard dichromate, a slight excess of the dichromate solution being added. Ammonium fluoride and potassium iodide were again added and the determination finished by running a "hypo" titration. The readings were all changed to $N/10$ and the cc. $N/10$ Mohr's salt subtracted from the cc. $N/10$ dichromate, thus obtaining the cc. of $N/10$ "hypo" which would have been used if there had been no error in the determination. The relation of these values to the volume of "hypo" obtained experimentally is shown in Table II. The difference in practically every case is very small, and of no quantitative significance.

TABLE II

(A) Cc. Mohr's Salt $N/10$	(B) Cc. $K_2Cr_2O_7$ $N/10$	(C) Cc. $Na_2S_2O_3$ Actually Used $N/10$	Cc. $N/10$ "Hypo" Which Should Have Been Used (B — A)	Cc. Difference
15.00	20.00	5.07	5.00	+0.07
21.14	27.86	6.72	6.72	0.00
25.60	31.38	5.88	5.78	+0.10
30.47	35.89	5.44	5.42	+0.02
36.42	41.57	5.12	5.15	—0.03

USE OF THE METHOD WITH IRON ORES

STANNOUS CHLORIDE REDUCTION—The method was next tried out on a series of 10 iron ores. The first method employed used stannous chloride as a reducing agent, and was run as follows: An amount of the ore equivalent to 25 cc. of a $N/10$ solution is weighed out and dissolved in 20 cc. to 30 cc. of 1 : 1 HCl by heating on the hot plate for about 20 min. Stannous chloride is added to aid in dissolving the ore. When solution is complete, permanganate is added slowly until a yellow color of Fe^{+++} appears. Stannous chloride in very slight excess is now added, drop by drop, to a small volume at high temperature until the solution is colorless. The solution is then cooled, diluted to about 200 cc. and 10 cc. of a saturated solution of mercuric chloride is added. An excess of standard $K_2Cr_2O_7$ is then run in, and 4 to 5 g. of ammonium fluoride added. After adding 5 g. of potassium iodide, and allowing it to dissolve, the liberated iodine is taken up with standard thiosulfate. The cc. of $N/10$ "hypo" are subtracted from the cc. of $N/10$ dichromate and the iron calculated.

The results first obtained by this method ran uniformly high as is shown in Table III.

TABLE III

SAMPLE No.	SAMPLE G.	$K_2Cr_2O_7$ 0.0965 N Cc.	$Na_2S_2O_3$ 0.1077 N Cc.	Fe by Modified Method Per cent	Fe by Regular Dichromate Method Per cent
1.....	0.6040	30	6.50	20.28	20.11
2.....	0.5034	20	2.30	18.66	18.15
3.....	0.5050	20	4.00	16.57	16.02
4.....	0.5040	20	3.50	17.21	16.58
5.....	0.6036	30	11.64	15.21	14.62

DETERMINATION OF THE CAUSES OF THE INACCURACY—One cause of these high results was probably the action of the iodine on calomel, oxidizing it to the mercuric condition

$$Hg^{+} + I^{\circ} \longrightarrow Hg^{++} + I^{-}.$$

In order to establish this point more definitely, a number of 25 cc. samples of a Mohr's salt solution were measured out and oxidized to the ferric condition with permanganate, then reduced with stannous chloride, adding different amounts of the salt in excess. These ferrous iron solutions were then analyzed by the modified method as outlined above. The following are sufficient to show the results of this investigation:

1—Practically no excess of $SnCl_2$
Stannous chloride was added until the solution was colorless
$K_2Cr_2O_7$ = 36.68 cc. $N/10$ solution
$Na_2S_2O_3$ = 11.61 cc. $N/10$ solution
25.07 cc. $N/10$ $K_2Cr_2O_7$ to oxidize Fe^{++}

2—One drop in excess of $SnCl_2$
$K_2Cr_2O_7$ = 30.90 cc. $N/10$ solution
$Na_2S_2O_3$ = 5.68 cc. $N/10$ solution
25.22 cc. $N/10$ $K_2Cr_2O_7$ to oxidize Fe^{++}

3—Four drops in excess of $SnCl_2$
$K_2Cr_2O_7$ = 30.90 cc. N/10 solution
$Na_2S_2O_3$ = 5.07 cc. N/10 solution
25.83 cc. N/10 $K_2Cr_2O_7$ to oxidize Fe^{++}

4—Eight drops in excess of $SnCl_2$
$K_2Cr_2O_7$ = 30.90 cc. N/10 solution
$Na_2S_2O_3$ = 3.72 cc. N/10 solution
27.18 cc. N/10 $K_2Cr_2O_7$ to oxidize Fe^{++}

When the potassium iodide is added it reacts with the Hg^{++} in solution causing the precipitation of red mercuric iodide. This precipitate, however, immediately reacts with the potassium iodide, forming the soluble and colorless $HgI_4^{=}$, which does not interfere with the end-points.

The potassium iodide also reacts with the precipitated calomel, changing it first to mercurous iodide, which breaks down into mercuric iodide and mercury.

$$2HgI \longrightarrow HgI_2 + Hg$$

This mercuric iodide then dissolves.

$$HgI_2 + 2I^- \longrightarrow HgI_4^{=}$$

As a result of this action there is left only a fine, gray precipitate of metallic mercury which remains during the titration.

Other investigators[1] have called attention to a similar effect of calomel on the permanganate titration in the Zimmerman-Reinhardt method. Barnebey[2] states that in the presence of a large amount of chlorides calomel interferes with a successful permanganate titration, and that the end-point becomes more indefinite and transient as the amount of calomel present is increased. Barnebey also states that in some cases the precipitated calomel completely disappeared.

REDUCTION WITH A MINIMUM AMOUNT OF STANNOUS CHLORIDE—The analysis of the iron, ores was repeated, using, so far as could be estimated, just enough stannous chloride to reduce the ferric iron, leaving practically no excess in solution. Although one investigator could not so regulate the addition of stannous chloride as to get concordant and correct results, a second analyst handled the method entirely satisfactorily, checking standard iron ores within 0.05 per cent with little difficulty. Some of his results compared with results of the straight dichromate method are given in Table IV.

TABLE IV

SAMPLE No.	WT. SAMPLE	$K_2Cr_2O_7$ Cc.	Normality $K_2Cr_2O_7$	$Na_2S_2O_3$ Cc	Normality $Na_2S_2O_3$	Fe Modified Method Per cent	Fe Straight Dichromate Per cent	Difference in Per cent
2	0.6000	29.18	0.1030	10.39	0.1010	18.19	18.15	+0.04
3	0.6000	30.00	0.1030	13.48	0.1010	16.09	16.02	+0 07
4	0.6000	30.00	0.1002	12.45	0.0994	16.42	16.58	+0.16
5	0.6000	30.00	0.1002	14.40	0.0994	14.65	14.62	+0.03
6	1.0000	30.00	0.1002	3.05	0.0994	15.09	15.12	—0.03
7	0.5000	18.02	0.0986	5.78	0.0989	13.49	13.44	+0 05
8	0.5000	19.15	0.0986	7.47	0 0989	12.74	12.71	+0.03
9	1.0000	30.00	0.1002	12.03	0.0994	10.11	10.01	+0.10
10	0.5000	18.53	0.0986	8.61	0.0989	10.89	10.84	+0.05

USE OF JONES REDUCTOR—When the Jones reductor was used to reduce the iron the method proved to be entirely satisfactory and correct results were easily obtained. The procedure here is very simple. The ore was dissolved in 30 cc. of 1 : 1 HCl without the addition of stannous chloride. It was then diluted to about 150 cc. and reduced by slowly running through a Jones reductor, taking the usual precautions. An excess of standard dichromate was run into the solution, ammonium fluoride and potassium iodide added, and the titration carried out as before. The volume titrated was about 350 cc. Definite and permanent end-points were reached. The results may be found in Table V.

TABLE V

ORE No.	SAMPLE G.	$K_2Cr_2O_7$ 0.1028 N Cc.	$Na_2S_2O_3$ Cc.	Normality $Na_2S_2O_3$	Fe Modified Dichromate Method Per cent	Fe Straight Dichromate Method Per cent	Difference in Per cent
1	0.6050	30	9.10	0.0987	20.15	20.11	+0.04
2	0.6056	30	11.28	0.0987	18.18	18.15	+0.03
3	0.6046	30	13.55	0.0987	16.10	16.02	+0.08
4	0.6048	30	12.90	0.0987	16.67	16.58	+0.09
5	0.6056	30	15.05	0.0990	14.70	14.62	+0.08
6	0.6043	30	14.40	0.0990	15.31	15.12	+0.19
7	0.6041	30	16.35	0.0990	13.56	13.44	+0.12
8	0.6053	30	17.22	0.0990	12.70	12.71	—0.01
9	1.0050	30	12.75	0.0990	10.12	10.01	+0.11
10	1.0033	30	11.38	0.0990	10.86	10.84	+0.02

HYDROGEN SULFIDE REDUCTION—The reduction of the iron with hydrogen sulfide was found to be unsatisfactory. The end-point was not permanent, and the results were entirely unreliable. A heavy precipitate of sulfur was of course obtained, and this may have been one of the causes of the trouble It was also noticed that a careful regulation of the concentration of H^+ seemed to be essential for a successful reduction of iron.

STANDARDIZATION OF METHOD

AMOUNT OF SAMPLE—The weight of sample should in each case be such as to have an iron content of about 25 cc. of an N/10 solution, or about 0.13975 g. of iron.

AMOUNT OF HYDROCHLORIC ACID—When the ore was dissolved in 20 to 35 cc. of 1 : 1 HCl, concordant results and permanent end-points were obtained. When 40 cc. or more of 1 : 1 HCl were used the end-points were not permanent, the blue color returned and low results were obtained. Too high a concentration of H^+ breaks up the ferric fluoride complex and causes iodine to be liberated, thus giving low results.

POTASSIUM IODIDE—Good checks were obtained when 3, 4, 5, or 6 g. of potassium iodide were added. Five grams is probably the most satisfactory amount of the reagent. When stannous chloride is used as a reducing agent, this larger amount is essential owing to the reaction between Hg^{++} and the I^-.

AMMONIUM FLUORIDE—Two and three grams of ammonium fluoride gave low results. Four and five grams gave correct, concordant results. Five grams seemed to be the best amount of the reagent to add. An equivalent amount of hydrofluoric acid can be substituted.

VOLUME OF SOLUTION—The volume of the solution at the completion of the titrations was about 250 cc. when the stannous chloride reduction was used. The volume was 350 cc. when the Jones reductor was used. This larger volume was made necessary by the washing of the reductor after reducing the iron.

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[1] Meinke, *Z. öffent. Chem.*, **4**, 433.

[2] Barnebey, *J. Am. Chem. Soc.*, **36** (1914), 1429.

CONCLUSIONS

The modified dichromate method as outlined above makes use of an exceedingly stable oxidizing salt which can be obtained in a very pure condition. The indicator employed is very delicate and affords an easily obtainable end-point. The method is more rapid than the straight dichromate method, and quite accurate. There seems to be no reason why it cannot be successfully used in commercial work.

INDICATORS AND THEIR INDUSTRIAL APPLICATION[1,2]

By H. A. Lubs

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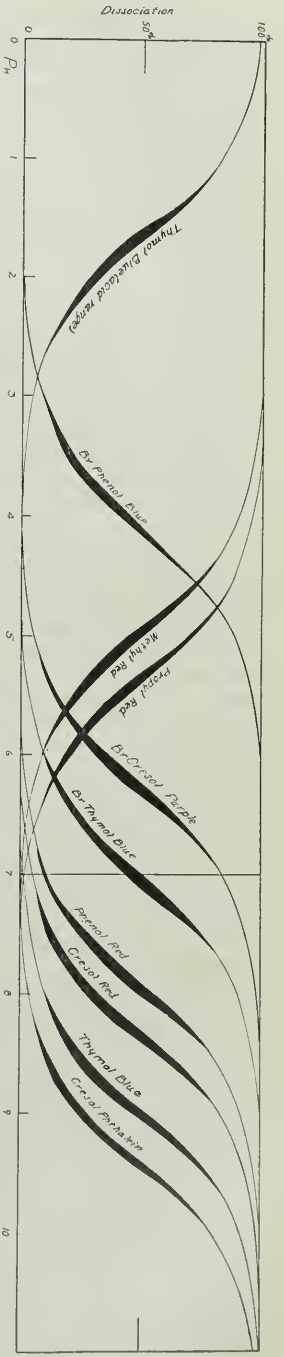
Perhaps no single operation of the various procedures necessary in general chemical manipulation can be considered of greater importance than that of acidimetric or alkalimetric titrations; yet in spite of this fact the subject of indicators is given but scant attention in the majority of our undergraduate colleges and universities.

The most recent and useful developments in the field of indicators have arisen from the increasing recognition by chemists and biologists of the great influence which the degree of acidity or H^+-ion concentration has upon various biological processes. In order to select the most brilliant and sensitive indicators for the colorimetric determination of H^+-ion concentration in certain biological fluids, Sorensen and his co-workers[3] at the Carlsberg Laboratory in Denmark investigated over one hundred dyes, determining the zones over which they changed, their brilliancy, and the effect of salt, protein, and protein decomposition products on their changing points. At the same time a great improvement was made in the preparation of standard solutions of known H^+-ion concentration for colorimetric work. Some years later Rowntree,[4] as a result of his physiological studies at the Johns Hopkins Medical School, suggested the use of phenolsulfophthalein, a compound not described by Sorensen, as a useful indicator for the determination ion of the H^+-ion concentration of blood. This indicator had been synthesized a number of years before by Sohon,[5] a student of Remsen, and subsequently studied by Acree and co-workers from the standpoint of the quinone-phenolate theory of indicators.

After a careful consideration of the work of Sorensen and others on indicators and upon investigating a very large number of compounds, it soon became evident that the synthesis of new, brilliant, and sensitive indicators would assist materially in a solution of the biological problems in which Dr. W. M. Clark, of the Bureau of Animal Industry, and the writer were interested. Having in mind the brilliancy of phenolsulfophthalein and knowing from the quinone-phenolate theory of indicators as developed by Acree[1] and his co-workers, that by suitable variations in the phenolic residue of a sulfophthalein dye there could be produced great variations in the dissociation constants of this group of indicators, it occurred to us that the synthesis of new compounds of this type should meet the need for sensitive and brilliant indicators covering a wide range of H^+-ion concentration.

After about two years of work we were successful in obtaining a series of new and brilliant indicators which left little to be desired for H^+-ion concentration between 10^{-1} and 10^{-10}. This series of indicators and the ranges over which they change is graphically shown in the accompanying chart already published by Clark and the writer.[2]

Reference to this chart shows that the new series covers a range from P_h^+1 to P_h^+10. The useful working ranges are indicated by the heavily shaded portions of the curves. P_h^+ is merely a convenient mode



Dissociation Curves of Indicators Considered as Simple Mono-Basic Acids, Showing Percentage Color Change with P_H (Shaded Portions of Curves Indicate the Useful Ranges) of expressing H^+-ion concentration and is the negative log of the H^+-ion concentration. In other words, $P_H{}^+2$, for instance, is equivalent to a H^+-ion concentration of 10^{-2}, or approximately that of 0.01 *N* hydrochloric acid. $P_H{}^+7$ is the neutral point. With the exception of methyl red, propyl red, and cresolphthalein, all of the compounds listed on the chart are of the sulfophthalein series.

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[1] Paper read at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

[2] Published by permission of the E. I. du Pont de Nemours & Co., Wilmington, Del.

[3] *Compt. rend. trav. Lab. Carlsberg*, **7** (1909), 1; **9** (1909), 1; *Biochem. Z.*, **21** (1909), 131, 209; **51** (1913), 307; *Ergebn. Physiol.*, **12** (1912), 393.

[4] *Archiv. Intern. Med.*, **16** (1915), 38.

[5] *Am. Chem. J.*, **20** (1898), 257.

[1] *Science*, **42** (1915), 101. Dissertation by E. C. White, Wisconsin, 1915. For further references see paper by White and Acree, *J. Am. Chem. Soc.*, **40** (1919), 1190.

[2] *J. Bact.*, **2** (1917), 1, 109, 191.

The uses of this series of indicators in titrations and in general chemical manipulations are numerous but only a few cases applying to the dye industry will be discussed.

Ordinarily, one does not think of any connection between the formation of azo dyes and hydrogen-ion concentration, but in certain cases coupling takes place with great readiness in acid solution, while in other cases a neutral or alkaline reaction is desirable. The speed of coupling can often be increased, and in certain cases the shade of the finished dye influenced by careful control of this factor. By judicious use of one or more of these indicators the degree of acidity or alkalinity of the reaction medium may be kept within closely defined limits and a more uniform product obtained.

In the isolation of certain intermediates, the intelligent application of indicators will be of great service. For instance, in the precipitation of an amphoteric substance like anthranilic acid from its alkaline solution, insufficient mineral acid incompletely precipitates the organic acid while too much mineral acid redissolves it. One can stop at exactly the right point by making spot tests from time to time on paper saturated with the proper indicator. By the addition of mineral acid until an acid reaction is obtained with methyl red, the end-point is approached, and by continuing the addition of acid until an acid reaction is shown by thymol blue, the point of maximum precipitation is reached.

Fractional precipitation is a very old procedure for the separation and purification of organic and inorganic compounds. By use of the proper indicator or indicators in acidifications, tars and other impurities can often be eliminated before precipitating the desired intermediates.

It is well known that certain dyes are very sensitive to acids or alkalies, especially upon drying, thereby causing undesirable effects on the shade of the finished product. In such cases the use of the proper indicators in neutralization would eliminate the possibility of an excess of the harmful constituent and facilitate the production of uniform products.

One of these new indicators, thymolsulfophthalein, has such interesting and unique properties as to merit special mention. Since it shows brilliant and sharp changes over two widely separated working ranges, thymolsulfophthalein serves the same purpose as a combination of two indicators. Hence it is an ideal substance for controlling such an operation as the liming of benzene or naphthalene sulfonation mixtures. So long as a test portion gives a red coloration with this indicator there is still free acid present; when the indicator shows a yellow color, the end-point is approached and the addition of lime can then be made very cautiously until a blue coloration, showing alkalinity, is produced. In this one substance we have practically a combination of Congo red and phenolphthalein. The acid change, however, occurs at a slightly higher H^+-ion concentration than that of Congo red. The use of this indicator in various acidimetric and alkalimetric titrations has already been described.[1]

In a recent article on indicator test papers, Kolthoff,[2] of Utrecht, states that phenolphthalein paper reacts very slowly unless the spot is rubbed with a glass rod, and suggests that this difficulty may be due to the fact that phenolphthalein crystallizes out on the paper. His conjecture is probably correct. Such trouble would not be encountered in the use of thymolsulfophthalein on account of its greater solubility in water.

Although litmus is the most extensively used of all indicator test papers, it is also the most unreliable.[3] Being a natural product and a mixture of substances, its purity and consequent sensitiveness varies with the mode of preparation. Upon examining specimens of litmus paper from a number of different manufacturers, one of the laboratories of the du Pont Company found that the product of only one concern was uniformly sensitive. As a substitute for litmus either of two indicators of the sulfophthalein series can be used, namely, dibromocresolsulfophthalein or dibromothymolsulfophthalein. The former changes from yellow to a brilliant purple, and the latter from yellow to a brilliant blue. Both can be obtained in very pure condition and consequently a uniform product is assured.

In conclusion it may be stated that for general laboratory use, if only two indicators are to be selected, methyl red and thymolsulfophthalein will be sufficient for most of the titrations and rough controls which the average chemist needs to make. The complete series, however, would be desirable when the highest precision and accuracy are to be attained. A more general and intelligent use of indicators will surely be productive of increased efficiency in many industrial operations.

THE ACIDIMETRY OF RED WINES AND FRUIT JUICES

By Alex. M. Macmillan and Alfred Tingle

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Received September 19, 1919

The method usually adopted for the determination of "total acids" in red wine and allied juices depends essentially on titrating 25 cc. of the sample with *N*/10 sodium hydroxide solution, using litmus paper as an indicator. That litmus paper is not a really desirable indicator is generally admitted; it is employed only for want of a better. In working with white wines phenolphthalein is always substituted, the color of the wine in such cases not obscuring the end-point. Thus it happens that titrations of red and white wines are not strictly comparable, nor are the results obtained with red wines either very accurate or always strictly comparable among themselves, for different samples of litmus paper vary in sensibility. We have found that 0.4 cc. of $N/10$ alkali must be added to 25 cc. of distilled water before the resulting mixture gives an alkaline reaction with some of the red litmus paper used in this laboratory.

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[1] *J. Am. Chem. Soc.*, **40** (1918), 1443.

[2] *Pharm. Weekblad*, **56** (1919), 175; *Chem. Abs.*, **13** (1919), 1689.

[3] *J. Biol. Chem.*, **38** (1919), 55; *J. Am. Soc. Agron.*, **10** (1918), 180; *J. Am. Chem. Soc.*, **40** (1918), 796; *J. Agr. Res.*, **10** (1917), 105.

Being convinced that the large experimental error and the troublesome manipulation of test drops were alike avoidable, we resolved to use phenolphthalein, detecting the end point by the spectroscopic method which has already been described[1] as generally applicable to the acidimetry of colored solutions.

One of us had already received a private communication to the effect that this method had failed when applied to wine lees. It appeared, however, that this failure was due, at least in part, to the fact that the analyst had not sufficiently adapted the working details to meet his individual case. Perhaps the principles on which modifications should be based were not enunciated with sufficient clearness in the original communication.

We have determined the conditions under which red wines and fruit juices can be spectroscopically titrated, and believe the method is both more rapid and accurate than that commonly used.

DETAILS AND RESULTS OF THE TITRATIONS

The wine or juice to be examined (25 cc.) is introduced into the titration vessel, followed by (approximately) 75 cc. of water. If desirable the wine may be first measured into an ordinary flask in which it can be heated, after which it is washed into the titration vessel with the water necessary for dilution. $N/10$ sodium hydroxide is then rapidly added from a burette until the end-point is near. This may be known either by the change in the natural coloring matter or by a previous rough titration. Phenolphthalein (2 cc. of one per cent solution) is next added, and the titration is continued with ordinary caution, the liquid being examined before a small spectroscope after each addition of alkali. The end-point is shown by the sudden appearance of the absorption band characteristic of alkaline phenolphthalein. It lies in the green region of the spectrum, very close to the yellow. In the absence of bright sunlight, any steady good batswing gas burner will be a satisfactory source of illumination.

The thickness of liquid suitable for observations at the dilution specified is 30 to 35 mm. Vessels of the necessary capacity, but of such shape as to give so thin a layer of liquid, are not usually made for chemical work. We found it convenient to perform our titrations in 6 oz. bottles shaped like pocket flasks and originally used for retailing small quantities of whisky or rum. The sides of such bottles are not parallel and are made of quite inferior glass, but these facts do not interfere in any way with the necessary observations.

The results we have obtained on a variety of samples, the conditions of successful titration, and the agreement *inter se*, of different titrations made on the same material, are tabulated below:

Nature and Condition of Sample	NaOH Solution ($N/10$ Required) Cc.
Port Wine—A 25 cc. wine + 75 cc water + 2 cc. phenolphthalein.......	20.7 20.8 20.8
Grape Juice—A 25 cc. juice + 75 cc. water + 2 cc. phenolphthalein.......	32.8 32.8 32.8
Port Wine—B 25 cc. wine + 75 cc. water + 2 cc. phenolphthalein.......	16.6 16.6 16.7
Grape Juice—B 25 cc. juice + 75 cc. water + 2 cc. phenolphthalein.......	41.8 41.7 41.6 41.8
"Medicated Red Wine" 25 cc. wine + 75 cc. water + 2 cc. phenolphthalein.......	14.8 14.6 14.6
"Raspberry Vinegar" 25 cc. juice + 50 cc. water + 2 cc. phenolphthalein.......	55.6 55.6 55.5

In each case, thickness of liquid examined = 30 to 35 mm.

It will be observed that less water was added before titration to the "raspberry vinegar" than to the other samples. This was not only because the juice was less deeply colored, but also because it was much more acid. The larger volume of standard alkali solution required brought the dilution at the end-point to the desired amount. Some wines which we have examined required much greater dilution than those mentioned above. In one case in our experience, 300 cc. of water were added.

REMARKS ON THE PRINCIPLES UNDERLYING SPECTROSCOPIC TITRATIONS AND THEIR PRACTICAL APPLICATION

Experience in this laboratory has shown that the spectroscopic method of detecting the end-point in acidimetry is often useful. It is capable of giving exact results in many cases where a very wide limit of error would otherwise be unavoidable.

No apparatus is required but such as should be found in any analytical laboratory and is used for many other purposes. But the successful application of the method depends on observing the conditions demanded by each individual case. No set of working rules can be laid down which would meet every analysis to be performed. Success can be obtained only by remembering the general principles on which the method is based, and deducing therefrom the experimental details which will meet individual requirements.

These general principles do not seem to have been made quite plain in the original description of the method,[1] but it seems reasonably apropos to consider them here.

The fundamental principle is that for many indicators there is an easily detected difference in absorption spectrum, according to whether the solution is acid or alkaline, and that the transition point can be readily recognized spectroscopically. But this difference, and therefore the neutral point, can be seen only when that part of the spectrum in which it occurs is not obscured by absorption bands due to the coloring matter originally present in the liquid to be titrated, and when the "effective concentration"[1] of the indicator itself is great enough to show the characteristic change distinctly.

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[1] *J. Am. Chem. Soc.*, **40** (1918), 873.

[1] *Loc. cit.*

A liquid too highly colored for titration by ordinary methods can almost always be rendered amenable to spectroscopic titration by reducing the effective concentration of its coloring matter. This may be done either by diluting with a solvent or by decreasing the thickness of the layer to be spectroscopically observed. A combination of these two methods is most generally useful. But if the amount of indicator added remains constant, its effective concentration is reduced at the same time and a point may thus be reached where it is so small that the spectroscopic change is obscured. More indicator must then be added. On the other hand, the effective concentration of such an indicator as cochineal must not exceed a certain amount. In fact, there is a connection between the quantity of indicator which should be used, the thickness of liquid observed, and the total volume of liquid present at the end-point.

This is not a novel principle, since it holds good for titrations conducted in the ordinary way, and is commonly, but rather vaguely, recognized. Its observance and application are essential when the spectroscope is used.

As regards the spectroscopic sensitiveness of phenolphthalein, we have noted that the end-point was strongly shown when 0.15 cc. of $N/10$ alkali was added to 100 cc. of distilled water containing 2 cc. of one per cent phenolphthalein solution, the thickness of liquids observed being 30 to 35 mm.

We have also found that when for any reason the effective concentration of the original coloring matter cannot be so reduced as to give an entirely bright and unimpeded light in that region of the spectrum where the absorption band of the indicator is situated, the latter band can often still be observed, provided the effective concentration of the indicator is increased, *i. e.*, a dark band may be superposed on a relatively light one.

Since the spectroscopic method of titration was first described, additional experience has been gained in the use of direct vision spectroscopes of different designs. An instrument may have too high, as well as too low, dispersive power for convenience. The "Beck-Thorp Patent Reading Pocket Diffraction" instrument seems best designed in this respect, and has the additional advantage that its "luminous pointer" measuring device enables the necessary readings to be taken more quickly and accurately than with an illuminated scale or with cross wires.

We have also conducted certain experiments on methyl red as an indicator for use in connection with the spectroscope, and find it well adapted to the purpose if in sufficient concentration. When the total volume of titrated solution is about 100 cc. and the thickness observed is 45 to 50 mm., 3 cc. of 0.05 per cent methyl red solution give a strong absorption band in the green region while the solution is acid. This band disappears entirely and sharply at the point which marks neutrality for this indicator. The titration readings in $N/10$ solution are the same as those obtained by the naked eye when a smaller quantity of methyl red is employed in an otherwise colorless solution.

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[1] The term "effective concentration" has been found a convenient one in this and similar connections where optical methods of analysis are under discussion. It is dependent not only on the relative amounts of solvent and active solute, but also on the thickness of the layer of solution observed, and sometimes on other factors. As applied to polarimetric observations, two sugar solutions of the same concentration, examined under otherwise identical conditions but in tubes of different lengths, would vary in "effective concentration" directly as the length of the tubes.

THE DeROODE-PERCHLORIC ACID METHOD FOR DETERMINING POTASH[1]

By T. E. Keitt

Laboratory of the Georgia Experiment Station, Experiment, Ga.

Increasing industrial needs and the limited supply of platinum make a substitute for that element in the determination of potash more and more imperative.

Of all the reagents suggested as substitutes perchloric acid seems the most promising. A study of available literature on this subject indicates that there are three substances that must be removed to secure concordant results: sulfates, ammonia, and organic matter. The sulfates may be removed by precipitating with $BaCl_2$ solution before making to volume, and the DeRoode moist combustion removes ammonia and organic matter. Using the DeRoode method of combustion the writer has done a small amount of work with perchloric acid as the reagent and makes this as a preliminary report, hoping that others will try it out and give him the benefit of their experience with the method.

PROCEDURE

Place 2.5 g. of the sample on a 12.5 cm. filter paper and wash successively with portions of boiling water into a 250 cc. flask until the washings amount to about 200 cc. Acidify the solution with 5 cc. of conc. HCl, while hot, precipitate the sulfates by adding drop by drop, in slight excess, normal $BaCl_2$ solution acidified with HCl (10 cc. usually suffice). Cool, make to mark, and shake. Allow the precipitate to settle. Transfer a 50 cc. aliquot part, corresponding to 0.5 g., to a 175 cc. porcelain evaporating dish, add 30 cc. of aqua regia and evaporate to dryness on hot plate; add a second portion of 30 cc. of aqua regia and evaporate to dryness; then add about 10 cc. of conc. HCl and 20 cc. of distilled water and evaporate to dryness. Dissolve in 20 cc. of hot water and add 5 cc. of perchloric acid, 1.12 sp. gr.; evaporate on hot plate or steam bath until copious fumes come off, remove and run the liquid around the bottom of the dish, and if it does not solidify on cooling, evaporate more and cool again. It can be rapidly cooled by floating the dish on cold water. Take up the residue with 5 cc. of cold water and add a second portion of 5 cc. of perchloric acid; evaporate the solution until dense fumes of perchloric acid appear. In case the residue appears baked, repeat the last operation. After *cooling*, add 20 cc. of 95 per cent alcohol, stir, and allow to stand 30 min. The precipitate may be collected either on a Gooch crucible carrying a pad of asbestos $^1/_8$ in. thick or on a tared filter paper. When the latter is used a good quality 7 cm. filter suffices. The collection of the precipitate on a tared filter is generally more rapid. In either case wash the precipitate twice with 95 per cent alcohol containing 0.2 per cent perchloric acid, transfer the precipitate using the same wash, and wash until the filtrate and washings amount to about 75 cc. Finally, wash twice with alcohol-ether (1 : 1), using 3 to 5 cc. each time, to remove all of the perchloric acid. Dry for 30 min. at 120° C. Weigh and dissolve the potassium perchlorate from the gooch with about 200 cc. of hot water. Use another receiver and wash the pad with alcohol or ether to facilitate drying, dry 30 min., and weigh. The loss is potassium perchlorate, and potassium oxide is calculated using factor 0.34. Where the tared paper is used no reweighing is necessary.

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[1] Presented at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 4, 1919.

The following table summarizes the analytical data accumulated in this connection:

TABLE I—ANALYTICAL DATA

FORMULA	Source of Nitrogen	Lindo-Gladding	DeRoode	DeRoode-Perchloric
PK............	None	3.51	3.46	3.26
PNK..	Cottonseed meal	1.70	1.78	1.65
PNK..........	Organic	4.68	4.70	4.66
PNK..........	Inorganic	4.26	4.41	4.38
PNK...... ...	Inorganic	4.45	4.74	4.59
PNK..........	Inorganic	3.91	4.02	3.86
PNK..........	Inorganic	4.05	4.10	4.14

While the data arc meager the results seem to justify further study along this line.

The writer proposes to make a more complete study along this line to be presented with the referee's report to the A. O. A. C. and will appreciate the experience of others in this connection.

LABORATORY AND PLANT

PURIFICATION OF BENZOIC ACID BY FRACTIONAL CONDENSATION

By Max Phillips and H. D. Gibbs

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Received October 23, 1919

Ever since the process of manufacturing benzoic acid from toluene came into general use, considerable difficulty had been experienced in freeing the product from certain objectionable impurities. The main impurities of the crude benzoic acid are: compounds chlorinated in the ring, compounds containing side-chain chlorine, small amounts of benzaldehyde, and "tarry matter." From a commercial standpoint the most undesirable impurity and the most difficult one to remove by ordinary methods is the one consisting of compounds chlorinated in the ring. These compounds are thought to be objectionable from the physiological point of view when benzoic acid is used in food products.

In connection with the purification of phthalic anhydride, obtained by the catalytic oxidation of naphthalene, a very efficient and satisfactory method of purification has been developed in this laboratory, based on the principle of "fractional condensation." This process has been used with success not only in the laboratory but also in the plant. It was thought that an application of this method to the purification of benzoic acid might give interesting and instructive, even if not wholly satisfactory, results. With this purpose in view the experiments recorded here were carried out.

TABLE I—TIME AND TEMPERATURE OBSERVATIONS AND AIR INFLOW

	Run 1					Run 2					Run 3				
Duration of Experiment	3 Hrs. 10 Min.					5 Hrs.					3 Hrs. 45 Min.				
	Chamber 1 ° C.	Chamber 2 ° C.	Chamber 3 ° C.	Chamber 4 ° C.	Oil-bath ° C.	Chamber 1 ° C.	Chamber 2 ° C.	Chamber 3 ° C.	Chamber 4 ° C.	Oil-bath ° C.	Chamber 1 ° C.	Chamber 2 ° C.	Chamber 3 ° C.	Chamber 4 ° C.	Oil-bath ° C.
Temperatures of the various chambers and of oil bath taken every 15 min.	60	44	39	45	115	56	39	33	31.5	140	65	33	30	29	118
	64	42	37	34	165	57	39	30	28	140	80	46	35	33	178
	70	43	46.6	43	170	78	43	34	32	140	108	64	36	34	170
	80	44	37	34	180	96	45	34.5	32	140	108	57	35	32	172
	116	49	38	33.5	185	70	45	34	31	140	119	80	39	33	170
	122	50	38.8	33.5	190	96	49	32	29	140	117	83	39	34	172
	124	57	39.6	34	195	126	58	34	31.5	165	124	91	38	33	112
	124	105	43.2	36.5	200	113	65	34.5	31.5	165	122	97	38	33	166
	124	105	43.2	37	200	114	68	35	31	160	121	112	40	34	172
	120	105	42.2	35.5	200	124	86	34	30.5	165	121	120	41	34	180
	120	104	44.6	37.5	200	118	108	34	31	160	120	120	41	34	178
	108	92	42	34.5	200	118	102	33	30	165	120	120	41	34	170
	112	102	44	35	200	122	119	33	29	170	113	113	41.5	33.5	170
	...	...	....	....	...	116	115	32	29	170	121	114	41	33	160
	...	...	....	....	...	115	111	33	29	170	120	119	40	34	170
	...	...	....	....	...	112	108	32	29	170	118	115	42	33	178
	...	...	....	....	...	111	109	32	29	170	...	...	....	....	...
	...	...	....	....	...	108	103	33	29	170	...	...	....	....	...
	...	...	....	....	...	104	98	32	26	175	...	...	....	....	...
Total l. of air passed through apparatus			2822					5725					3615		
L. of air per min. (Average)			14.8					19					16		

MATERIAL

The crude benzoic acid was obtained from E. I. du Pont de Nemours and Company in a 10-lb. lot. It was of a grayish color, very moist, and had a decided benzaldehyde odor. It contained a small amount of foreign matter, such as paper, wood, and string.

APPARATUS

The apparatus (Fig. 1) used in these experiments

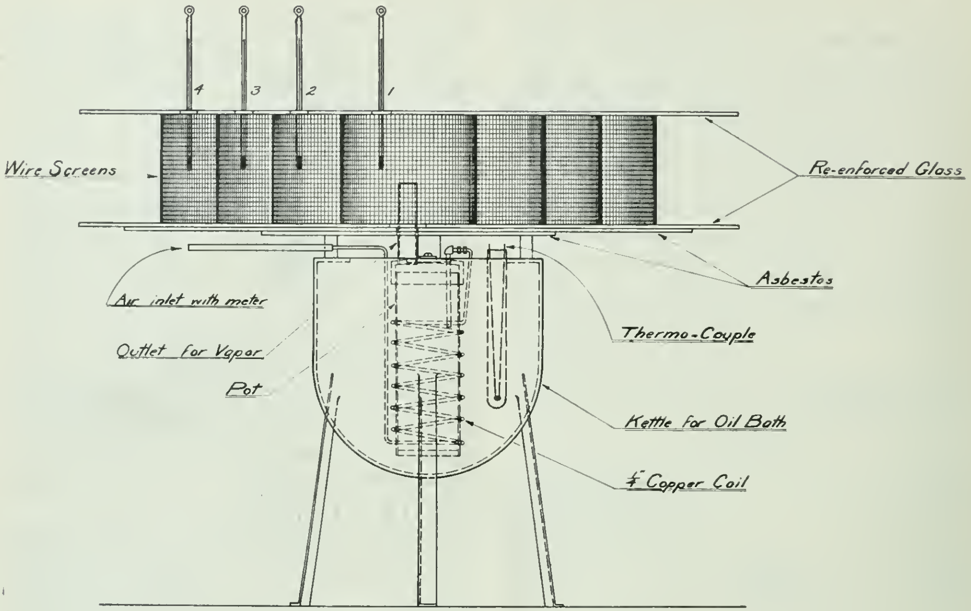

Fig. 1—Fractional Sublimation Apparatus

consisted of a kettle filled with lubricating oil, the temperature of which could be determined by means of a thermocouple. In this bath there was immersed a pot provided at the top with a 1-in. iron pipe, extending into Chamber 1 and serving as the outlet for the vapors. The pot was surrounded by a ¼-in. copper coil which terminated inside the pot. Air, measured by means of a gas meter, was passed through the copper coil and into the pot, and when the oil bath was at the proper temperature, this caused the material in the pot to volatilize and escape through the vapor outlet into Chambers 1, 2, 3, and 4, respectively. These chambers consisted of cylindrical wire screens, ¼-in. mesh, of different diameter, placed concentrically, and insulated from the heat of the oil bath by means of two sheets of asbestos and a thick reënforced glass plate, the latter serving also as a floor for the sublimation chambers. They were further insulated by a similar glass plate placed on the top of the screens. The temperature of each chamber was determined by means of a thermometer placed in the center of it, and thus the general gradation of temperature between the different compartments carefully noted.

METHOD

The pot was about ¾ filled with the crude benzoic acid and the chambers were heated by passing in a stream of hot air. When the temperature of the first chamber was about 50° to 60° and the oil bath about 120°, the air inflow in the chambers was discontinued and the air was passed at a definite rate through the copper coil and into the pot containing the benzoic acid. The benzoic acid thereupon sublimed and collected into the various chambers. Temperature readings of the oil bath and of each chamber were taken every 15 min. The experiment was discontinued when no more benzoic acid sublimed, and the weights of the sublimates in each chamber, as well as that of the residue remaining in the pot, were determined. Total acidity and chlorine determinations were made on the products and also upon the original benzoic acid. The chlorine was determined by Lemp and Broderson's[1] modification of the Pringsheim method. Altogether three runs were made. Run 3 differed from the other two in that air-dried benzoic acid was used instead of the wet material as obtained from the manufacturers. The dry material was found to be preferable to the other, in that losses, due to the steam distillation of the benzoic acid, were eliminated. The data obtained in these experiments are recorded in the accompanying tables.

Table II—Weight of Material

	Run 1 (Made with wet crude material)	Run 2 (Made with same material as No. 1)	Run 3 (Made with air-dried material)
Wt. of charge in g.	479.0	500.0	350.0
Wt. in g. in Chamber 1	47.0	50.0	20.0
Wt. in g. in Chamber 2	70.0	71.0	110.0
Wt. in g. in Chamber 3	2.5		5.5
Wt. in g. in Chamber 4	0.5		
Non-volatile residue (wt. in g.)	94.0	114.0	131.0
Wt. in g. lost in process	265.0	265.0	83.5
Per cent lost (other than residue)	55.3	47.0	23.8
Per cent of total obtained as sublimate	25.0	24.2	38.7

Certain advantages seemed to be gained by this method of condensing solids from a heated gas stream. The compartments separated from each other by screens or partitions containing a multitude of orifices

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[1] *J. Am. Chem. Soc.*, **39** (1917), 2069.

Table III—Analytical Data

	Original Material		Run 1 (Made with crude material)				Run 2 (Made with crude material)			Run 3 (Made with air-dried material)			
	Crude Benzoic Acid Per cent	Air-dried Material Per cent	Chamber 1 Per cent	Chamber 2 Per cent	Chamber 3 Per cent	Residue Per cent	Chamber 1 Per cent	Chambers 2, 3, and 4 Per cent	Residue Per cent	Chamber 1 Per cent	Chamber 2 Per cent	Chambers 3 and 4 Per cent	Residue Per cent
Moisture	41.2	3.5	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
Acidity expressed as benzoic acid	52.1	79.0	97.2	97.4	93.5	56.6	94.7	95.5	65.0	95.1	95.5	95.5	60.9
Total chlorine	4.45	5.46	1.48	1.49	1.51	8.28	2.53	1.02	8.49	1.65	0.34	0.34	7.92
Monochlorobenzoic acid, from total chlorine minus side-chain chlorine	14.1	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
Benzoic acid by difference, total acidity minus monochlorobenzoic acid	68.0	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
Chlorine in side-chain	1.25	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

maintain a temperature gradient in a remarkably constant manner, the moving stream of gases losing its heat gradually on passing through the orifices. The drop in temperature is sharp at the screens.

The screens, or orifices, afford condensing surfaces, greatly facilitating the formation of large crystals.

Though the screens have every appearance of acting as sieves, this is not their function, for the large size of the mesh prohibits such action. The crystallization seems to be due to the sudden drop of temperature of the gases on passing through the orifices, the metal screens acting as conductors of heat.

It is reasonable to expect a large scale apparatus to produce better results than the small laboratory experiments, since sublimations in general are better conducted on a large scale.

It is to be noted that the product obtained in Run 3, Chamber 2, from a very impure crude benzoic acid, was almost free of chloro-derivatives and a very pure benzoic acid resulted, the principal foreign substance present being about 4 per cent of water.

THE MANUFACTURE OF PHENOL IN A CONTINUOUS HIGH PRESSURE AUTOCLAVE

By Kirk Brown

Condensite Co. of America, Bloomfield, N. J.

Received September 9, 1919

Although condensite, a phenolic condensation product, and halowax, a chlorine substitution product, are the best known inventions of the late J. W. Aylsworth, they were but two of many that he produced in his short but fruitful life. The last work to which Aylsworth addressed himself before his untimely death in 1917 was the development of a continuous high pressure autoclave.[1]

Although many chemical reactions can be carried out with a great economy of time and material if conducted under high pressure and temperature, very little work of this character has been done except in laboratories on account of the difficulty and expense of producing, and the danger of operating, apparatus of the usual design involving the use of high temperatures and of pressures up to several thousand pounds per square inch.

DESCRIPTION OF AUTOCLAVE

The Aylsworth continuous autoclave consists essentially of a heated coil through which the reacting fluids are forced by means of pumps. The practicability of this apparatus depends very largely on the heating medium in which the reacting coil is immersed. If a liquid is used that must be put under pressure in order to attain the desired temperature, the apparatus must be heavily constructed and will cost correspondingly, and not be free from danger of explosion. Fusible metals can be used but have certain objectionable features, as have hot gases or vapor. A satisfactory medium should readily transmit heat by conduction; should be thinly fluid at the temperatures of operation so that it will circulate freely, thus transmitting heat by convection; should have a boiling point higher than the temperature to which the reacting materials are to be subjected, so that it need not be used under pressure; and should not attack metals, volatilize readily, or decompose.

Nitrite of soda was found to fulfill these conditions, its melting point being 415° F., and its boiling point 734° F. According to the description given in the literature, this substance decomposes at temperatures above its melting point, but baths have been maintained continuously at and above the boiling point for a number of weeks without the least evidence of decomposition.

MANUFACTURE OF PHENOL

In the manufacture of phenol from chlorobenzene in this autoclave, one tank contained the chlorobenzene and another the sodium hydroxide solution; the pump had two plungers of such relative size as to feed the required quantity of each of these liquids. This arrangement permitted the use of different packings, rubber for the alkali solution and leather for the chlorobenzene, thus avoiding the difficulty of providing a packing that would be attacked by neither.

The reacting ingredients, under a pressure of 2500 to 3000 lbs. per sq. in., were forced through a coil of extra heavy hydraulic pipe which was maintained at a temperature of 700° F. by a bath of nitrite of soda. The sodium phenylate thus formed was permitted to pass from the coil by a needle valve, the opening of which was so regulated as to maintain the proper pressure in the coil. This was only a question of proportion between the capacity of the pump and the area of the opening of the needle valve, and the time of passage through the coil of the reacting ingredients. From the coil, the sodium phenylate passed directly to a condenser where it was condensed; it was then acidified with hydrochloric acid and the resultant crude phenol distilled. The writer has seen crude phenol produced in this manner in 15 min., the reaction proper taking but a fraction of that time.

The entire process is simplicity itself; the apparatus much less in size and cost, and in space occupied, than that necessary in any other system used in the manufacture of phenol, and doubtless this statement applies with equal force to the manufacture of many other substances. Crude diphenyl ether, for example, was produced in the same manner and in almost the same time.

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[1] U. S. Patent 1,213,143.

At the time of Aylsworth's death, development work on the production of phenol had not proceeded far enough to say with certainty what proportion the final product would bear to the materials used, but there is little waste involved, for the unreacted materials can be recovered and again passed through the apparatus, and their quantity controlled by the time they are under reacting conditions, and this in turn by the size of the apparatus and the proportionate time used.

Theoretically, one pound of benzene should produce one pound of phenol. Moreover, the salt required to prepare the electrolytic chlorine used in the reaction is again formed, and could be recovered. Possibly, also, the hydrogen used in the electrolytic process might be used to furnish part of the heat for the reaction. A 100 per cent production, of course, is not possible, as there are unavoidable wastes in the electrolytic process and in the chlorination of the benzene, and also a very small loss in the conversion of chlorobenzene to phenol.

COMPARISON OF METHODS

Many methods of synthetic phenol manufacture have been developed.[1] A brief description of one method is given herewith for comparison with the Aylsworth process.

The ordinary method is as follows:

1—A mixture of sulfuric acid and benzene is allowed to react for 18 or 20 hrs. Benzenesulfonic acid is formed to the extent of about 60 per cent of the sulfuric acid taken. By the addition of oleum, containing 25 per cent sulfuric anhydride, to the diluted acid, more benzene is sulfonated, giving a total efficiency of about 80 per cent of the total sulfuric acid.

2—The benzenesulfonic acid is separated from excess sulfuric acid by treatment with lime. After filtering from calcium sulfate, the calcium benzenesulfonate is converted into the sodium salt by treatment with sodium carbonate. A considerable loss of the sodium salt occurs in the removal of calcium carbonate in a filter press.

3—The sodium benzenesulfonate is next evaporated to dryness, usually with multiple-effect evaporators.

4—It is then converted to sodium phenylate by fusion with an excess (about 75 per cent) of the theoretical molecular proportions of caustic soda. This excess is generally wasted, though it can be recovered economically when caustic is high in price by an elaborate apparatus, as described further on.

5—The fused mass is entirely dissolved in water and the solution is neutralized with acid, and allowed to stand while the phenol separates out. The latter is drawn off and distilled, and the balance of the solution (containing some phenol) is thrown away, but the sulfite of soda may be recovered if desired. Losses occur in distillation.

The Aylsworth method consists of the following steps:

1—Chlorobenzene and caustic soda react to produce sodium phenylate and salt.

2—The sodium phenylate and salt are neutralized with hydrochloric acid and the crude phenol and salt solution allowed to separate by settling.

3—By blowing steam through the salt solution an additional quantity of phenol is recovered.

The difference in the two methods is evident at a glance and as each step is carried out in a different unit of apparatus, the smaller size of the plant as a whole in the case of the Aylsworth method is also apparent. Not only is there less apparatus, but in nearly each instance the units of the Aylsworth apparatus are smaller because of the greater rapidity with which the work is done, thus making possible important economies in time, labor, floor space, capital investment, etc.; a cheaper acid is used and only about 5 per cent of the quantity, and about 40 per cent of the amount of caustic soda.

AN ELECTRIC HEATER FOR THE COAL-TAR NAPHTHA DISTILLATION TEST

By J. Bennett Hill and Richard B. Chillas

H. W. Jayne Laboratory, The Barrett Co., Frankford, Philadelphia, Pa.

Received October 29, 1919

The control of the plant operation of fractional distillation processes, particularly in the distillation of coal-tar naphthas, is generally carried out by observing the distillation range of samples of the distillate taken as it runs off the still. For this purpose the commonly used method is the distillation test, somewhat similar to the petroleum distillation method, and recently fully described by Weiss.[1] On account of the fact that this method requires the use of a gas flame, which in a benzol plant would be out of the question on account of the fire risk, it is necessary to send the samples to the laboratory to be tested. It would generally be not only much more convenient but also more economical to have them made on the spot. In order to avoid the risk of the flame, we have used a steam heater to a considerable extent in our benzol plant in carrying out the distillation tests. This device was, however, open to two objections: first, that the heating conditions of the flask were so decidedly different from those obtained with gas heating that the results were different, and, second, that only low boiling liquids could be tested. This paper describes an electric heating method which eliminates the fire risk and at the same time gives results identical with those obtained in the laboratory, using a gas flame.

Another type of electrical heater for distillation tests has recently been developed by the Bureau of Mines,[2] the idea of this being, however, to provide a cleaner and more nearly uniform heat rather than to cut down fire risk. A heater such as this with exposed hot wires could not be used in a building where inflammable vapors are present.

The heater selected for this work was an electrically

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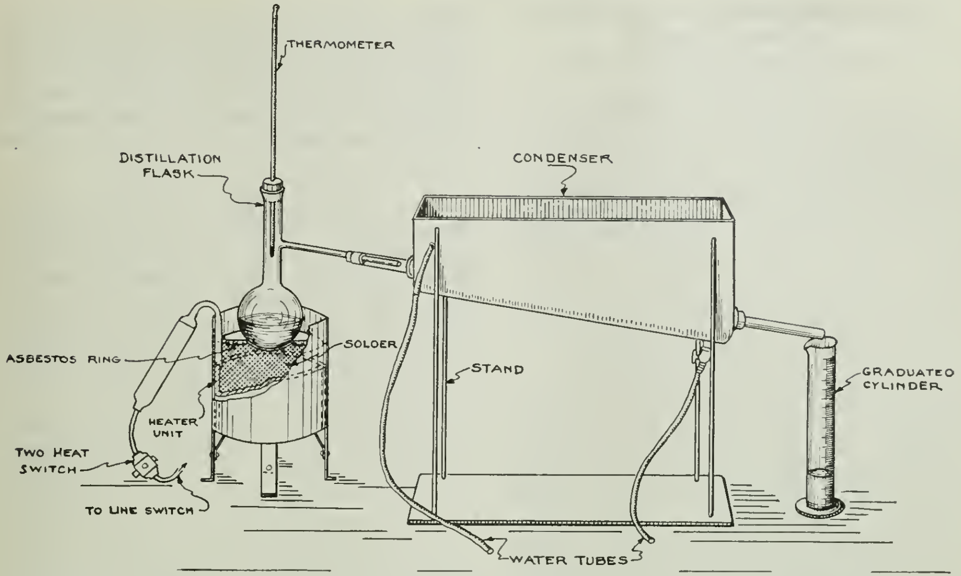
[1] *Met. Chem. Eng.*, **13** (1915), 686–690; **15** (1916), 185–192.

[1] This Journal, **10** (1918), 1006.

[2] E. W. Dean, *Ibid.*, **10** (1918), 823.



heated solder pot such as is on the market.[1] It consists of a cylindrical iron pot, 12.5 cm. in diameter and 10 cm. in height, with a heating unit suitably and completely enclosed, and entirely immersed, when in use, in the solder. The heating unit, cylindrical in form, 5.5 cm. in height, 10.5 cm. inside diameter, and approximately 7 mm. in thickness, rests on the bottom of the pot and is set slightly away from the wall in such a manner as to be completely surrounded by the solder. The pot is filled to within 3 cm. of the top by approximately 15 lbs. of 50 per cent lead-50 per cent tin solder. A heater appropriate to the lighting circuit voltage is used and by means of a switch the current can be varied between a low heat taking 400 watts, which will hold the temperature of the bath between 240° and 280° C., and a high heat taking 800 watts, which will hold the bath at a temperature of 345° to 380° C. With this device no part of the apparatus with a temperature higher than the solder itself is exposed to outside vapors.

Safety tests have been made by pouring benzene into the solder bath at both the low and high heats. No cases of ignition of the material have been obtained.

The general arrangement of the apparatus for the test is shown in the figure. A ring of asbestos board cut to fit the bath is floated on the surface of the solder and the heat supplied to the flask is regulated by the size of the circular hole in this pad and by the depth to which the flask is immersed in the molten metal. In practice the bath is always kept hot, the high or low heats being used according to the general class of substances to be tested, the low heat being sufficient for materials boiling up to about 180° C. To conduct the test the proper asbestos pad is floated on the solder, the sample of liquid introduced into the flask, the flask connected with the condenser apparatus and dipped into the molten metal through the hole in the pad. The rate of distillation can readily be adjusted to correspond to that obtained with the gas flame method.

Table I

	Solder Bath		Gas Flame	
	Test 1 ° C.	Test 2 ° C.	Test 3 ° C.	Test 4 ° C.
Pure Benzene				
Start	79.2	79.4	79.4	79.6
5%	79.8	79.8	79.8	80.0
50%	80.0	80.0	80.0	80.0
95%	80.6	80.4	80.5	80.4
Dry	80.6	80.6	80.6	80.6
Solder Temperature	265.0	242.0	...	...
Hole in pad, inches	1.5	1.5	...	...
Meta-Xylene				
Start	139.1	139.1	139.1	139.1
5%	139.5	139.3	139.3	139.3
50%	139.5	139.5	139.5	139.5
95%	139.8	139.5	139.8	139.8
Dry	139.9	139.9	139.9	139.9
Solder Temperature	245.0	265.0	...	...
Hole in pad, inches	2.0	2.0	...	...
Solvent Naphtha				
Start	135.0	135.0	136.0	136.0
5%	138.0	138.0	138.0	138.0
25%	141.0	141.0	141.0	141.0
50%	144.0	144.0	144.0	144.0
75%	149.0	149.0	149.0	149.0
90%	157.5	157.5	158.0	157.0
95%	164.0	164.0	...	166.0
Dry	173.0	171.0	174.0	174.0
Solder Temperature	250.0	245.0	...	...
Hole in pad, inches	2.0	2.0	...	...
Crude Cresylic Acid (95%)				
Start	195.0	195.0	195.0	195.0
25%	199.0	199.5	200.0	200.0
50%	201.0	202.0	202.0	202.0
75%	204.0	204.5	205.0	205.0
90%	209.0	209.5	211.0	211.0
Dry	223.0	222.0	223.0	223.0
Solder Temperature	340.0	350.0	...	...
Hole in pad, inches	2.0	2.0	...	...

A series of comparisons has been made of boiling ranges obtained by this method and those obtained by the standard gas flame distillation. These results, a few of which are shown in Table I, are practically identical.

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[1] Made by the Westinghouse Electric and Manufacturing Co.

THE MACMICHAEL TORSIONAL VISCOSIMETER[1]

By Winslow H. Herschel
Oil Laboratory, Bureau of Standards, Washington, D. C.

Received August 26, 1919

INTRODUCTION

A torsional viscosimeter is an instrument for determining the viscosity of a liquid by a torsional balance, usually consisting of two concentric cylinders, one of which has an angular motion about their common axis. One of the cylinders is suspended by a fine wire, thus forming a torsional pendulum. In some instruments, as for example the Doolittle,[2] readings are made of the retarding effect of the liquid when the pendulum is allowed to oscillate. In other instruments, of which the MacMichael[3] is an example, the outer cylinder is revolved at constant speed. The inner cylinder rotates until the torsional force in the suspending wire balances the viscous resistance, and then remains in a fixed position so that a reading may be taken. In the most accurate, so-called absolute, instruments, care is taken to avoid end effects, so that the instrumental constants necessary in calculating viscosity from the readings may be calculated from the dimensions.[4] With commercial instruments, such as the MacMichael, the construction may be simplified by permitting end effects. Instruments of this latter class must be calibrated by the use of liquids whose viscosity has been determined by absolute instruments of the torsional or other types.

DESCRIPTION OF MACMICHAEL VISCOSIMETER

The essential parts of the MacMichael viscosimeter are a motor-driven oil cup and a torsional pendulum suspended above the center of the cup by a fine piano wire. The pendulum consists of a tube enclosing the wire and carrying a disc at its lower end and a dial near the point of support. The disc is 60 mm. ($2^{5}/_{16}$ in.) in diameter and 5 mm. ($^{3}/_{16}$ in.) thick, and is immersed in the oil or other liquid to be tested. As the inside diameter of the cup is 70 mm. ($2^{13}/_{16}$ in.) there is ample clearance between the cup and the disc, and accurate centering of the pendulum in the cup is not required.

The dial is fastened to the tube by a tapered fit, and is graduated from 0 to 300 for reading the angular deflection of the pendulum. The zero setting is made roughly by turning the dial on the tube, and more accurately by movement of the pointer attached to the support of the pendulum. Since it is stated that the pendulum should not be allowed to make more than two revolutions, so as not to overstrain the torsion wire, the maximum reading is 600° M (MacMichael degrees).

The wires are about 254 mm. (10 in.) long and of three sizes, the speed being adjusted so that the smallest gives a deflection of 100° M, the second gives 10° M, and the third gives 1° M with 110 cc. of water at 20° C. (68° F.) in the cup. In the tests which are to be described, Instrument 6 was used with the medium-sized wire, 0.266 mm. (0.0105 in.) in diameter, and it was found that a speed of 114 revolutions per minute was necessary to get the above deflection. The speed control is of the phonograph type and adjustments are easily made by a thumb screw.[1]

POSSIBLE SOURCES OF ERROR

Since it is not necessary with a torsional viscosimeter to maintain a constant temperature over a considerable period of time, these instruments have a great advantage in speed of operation as compared with an efflux viscosimeter. This is especially noteworthy when it is desired to obtain a temperature-viscosity curve, it being necessary only to heat the oil to a maximum desired temperature, and to take the readings of temperature and of viscosity as it cools off. Even the labor of taking readings may be avoided by making the record autographic, as in the Hayes and Lewis viscosimeter.[2] There is, however, considerable question as to the correct method of calibrating a torsional viscosimeter so that its readings may be converted into absolute viscosities, or poises, for comparison with other instruments. Among the possible sources of error are turbulence, centrifugal force, and the effect of temperature in changing the length and diameter of the torsional wire, and thus changing the clearance between the disc and the bottom of the cup.

To estimate the error due to elongation of the wire, a rise of temperature of 80° C. (144° F.) was assumed. The elongation was found to be about 0.24 mm. (0.0095 in.) or only 4.8 per cent of the total clearance of 5 mm. ($^{3}/_{16}$ in.) between the bottom of the disc and the bottom of the cup. It will be shown later that only one-third of the deflection of the pendulum is due to viscous resistance below the disc and when this is taken into consideration the estimated error due to elongation of the wire would be reduced to 1.6 per cent.

The actual error would be considerably less because only one-fifth of the length of the wire is exposed to the temperature of the oil.[3] This question could not be investigated experimentally because the instrument at hand was not supplied with an electric heating coil, so that it was impracticable to work at temperatures above 55° C. (131° F.).

According to Hayes,[4] in the MacMichael instrument, "the lines of flow above and below the disc are spirals and not circles. This is due to the centrifugal action of the rotating liquid, and as a result an error is introduced due to the fact that the liquid undergoes acceleration. This error is not large." That spiral flow takes place is admitted by MacMichael who does not attempt to calculate viscosity from the dimensions of his instrument. He realized also that it was desirable to reduce the turbulence by "reducing the speed, reducing the dimensions of parts or increasing the viscosity of the fluid," and says: "For a standard testing fluid, a high grade neutral mineral oil of high viscosity, such as some of the medicinal oils now on the market, is suggested, this oil to be supplied in metal containers by the U. S. Bureau of Standards, or some other recognized authority."

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[1] Published by permission of the Director of the Bureau of Standards.

[2] *J. Am. Chem. Soc.*, **15** (1893), 173, 454.

[3] This Journal, **7** (1915), 961.

[4] M. Couette, *Ann. chim. phys.*, **21** (1890), 433; E. L. Harrington, *Phys. Rev.*, **8** (1916), 738; A. V. Bleininger and H. H. Clark, *Trans. Am. Ceram. Soc.*, **12** (1910), 383; M. D. Hersey, *J. Wash. Acad. Sci*, **6** (1916), 525; E. R. Drew, *Phys. Rev.*, **12** (1901), 114.

[1] For further details of the construction of the instrument see U. S. Patent 1,281,042, Oct. 8, 1918.

[2] *J. Am. Soc. Mech. Eng*, **38** (1916), 626, 1002, 1003.

[3] Compare "A Method for Measuring the Viscosity of Blast Furnace Slag at High Temperatures," A. L. Feild, U. S. Bureau of Mines, *Technical Paper* **157** (1916), 12.

[4] *Loc. cit.*

He also suggests the use of a cane-sugar solution of 7 parts by weight of sugar to 4 parts of cold water, but fails to state what deflection should be obtained with this liquid.

Eimer and Amend have published in *Bulletin* **211** comparative tests of the MacMichael and Saybolt Universal Viscosimeters which were made at the laboratory of the Standard Oil Company of California. Table I is calculated from the data there given, with the addition of the specific gravities of the oils which were kindly furnished by the Standard Oil Company.

TABLE I—COMPARISON OF READINGS OF MACMICHAEL AND SAYBOLT UNIVERSAL VISCOSIMETERS, ACCORDING TO MACMICHAEL

Sample Number			1	2	3	4	5	6
Baumé			21.7	21.4	21.3	20.6	20.1	19.7
Specific Gravity			0.924	0.925	0.926	0.930	0.933	0.936
TEMPERATURE ° F.	° C.							
60	15.6	S	366	419	517	1016	..	..
		R	1.906	1.724	2.085	2.082	..	..
70	21.1	S	262	331	357	673	1084	..
		R	1.858	1.994	2.111	2.083	2.098	..
80	26.7	S	191	238	259	467	706	1005
		R	1.818	1.888	1.963	2.140	2.108	2.250
90	32.2	S	144	177	190	323	484	658
		R	1.694	1.808	1.900	2.018	2.122	2.150
100	37.8	S	112	137	143	231	336	452
		R	1.648	1.757	1.811	1.975	2.100	2.142
110	43.3	S	92	108	113	175	254	326
		R	1.586	1.636	1.713	1.863	2.049	2.090
120	48.9	S	78	89	92	135	184	240
		R	1.592	1.589	1.615	1.777	1.898	2.050
130	54.4	S	67	75	77	109	142	183
		R	1.595	1.562	1.604	1.678	1.776	1.927
140	60.0	S	58	64	66	92	113	142
		R	1.610	1.561	1.610	1.672	1.713	1.844
150	65.6	S	53	57	58	77	96	112
		R	1.656	1.583	1.568	1.638	1.683	1.698
160	71.1	S	49	52	54	67	80	94
		R	1.690	1.625	1.635	1.634	1.632	1.678
170	76.7	S	46	48	49	59	69	80
		R	1.769	1.713	1.690	1.638	1.605	1.666
180	82.2	S	44	45	46	54	61	68
		R	1.833	1.731	1.703	1.687	1.605	1.619
190	87.8	S	42	43	44	50	55	61
		R	1.908	1.791	1.833	1.723	1.618	1.648
200	93.3	S	39	42	42	47	51	55
		R	1.950	1.909	1.909	1.808	1.700	1.667
210	98.9	S	38	39	40	44	47	50
		R	2.111	1.950	2.000	1.833	1.740	1.666

S—Time of flow in seconds, Saybolt Universal Viscosimeter.
R—Ratio of time, Saybolt, to MacMichael degrees.

It will be seen that the ratio of time, Saybolt, to MacMichael degrees decreases with the temperature of a given sample, except at high temperatures, and decreases as the specific gravity decreases, for a given temperature. It is, therefore, evident that the conversion factor changes with so many variables that a MacMichael-Saybolt conversion table is impracticable except for some assumed specific gravity.

THE DETERMINATION OF VISCOSITY IN POISES FROM MACMICHAEL DEGREES

If the effects of turbulence, centrifugal force, and other sources of error are neglected, the turning moment due to the viscous resistance of the layer of oil underneath the disc would be equal to:

$$T = \frac{\pi^2 \mu n D^4}{16h} \qquad (1)$$

where T = turning moment in kg. cm.
μ = viscosity in kg. sec. per cm².
n = revolutions per sec. of oil cup
D = diameter of disc in cm.
h = clearance below disc in cm.

A known turning moment was applied to the torsional pendulum and the torsional modulus of elasticity was calculated from the equation

$$G = \frac{4800Tl}{\pi^2 d^4 M} \qquad (2)$$

where G = torsional modulus of elasticity, in kg. per cm².
d = diameter of torsional wire in cm.
l = length of torsional wire in cm.
M = deflection of wire, in MacMichael degrees

Using the value of G = 880,000, *as found by test*, the measured values of d, l, h, and D, a speed of 114 r. p. m., and an assumed value of 1.4 poises = 0.000001428 kg. sec. per cm². for the viscosity,[1] it was found by combining Equations 1 and 2 that the theoretical deflection would be 119.7° M. From Fig. 1 the actual deflection for this speed and viscosity was 350° M, so that the calculated deflection is only 0.342 of the total. This shows the impossibility of calculating the deflection from the dimensions of the instrument. On this account, and also on account of the impracticability of manufacturing instruments in which the variations in the essential dimensions would be negligible, it is necessary that each operator should be able to calibrate his own instrument by the use of liquids of known viscosity.

TABLE II—TESTS OF MACMICHAEL VISCOSIMETER AT 114 REVOLUTIONS PER MINUTE

LIQUID	TEMPERATURE ° C.	TIME Sec.	DENSITY G. per Cm³.	VISCOSITY Poises	DEFLECTION MacMichael Degrees
20 per cent sucrose........	20	...	...	0.0196	15
40 per cent sucrose........	20	...	...	0.0620	32
60 per cent sucrose........	20	...	...	0.565	157
Oils, Saybolt viscosimeter..	15	54.3	0.858	0.0740	31
	20	50.1	0.855	0.0634	26
	25	48.4	0.852	0.0588	23
	25	97.3	0.871	0.1702	52
	25	114.6	0.894	0.2111	64
	25	171.5	0.883	0.3235	86
	20	323.4	0.872	0.615	170
	40	127.0	0.858	0.2272	65
	55	79.2	0.848	0.1284	50
	20	106.6	0.853	0.1855	61
	40	60.8	0.839	0.0874	36
	55	48.4	0.829	0.0574	27
	20	205.4	0.893	0.3955	125
	40	88.4	0.879	0.1530	55
	55	61.4	0.870	0.0921	40
	20	653.0	0.877	1.255	324
	40	239.2	0.863	0.447	128
	55	133.8	0.853	0.2395	75
Oils, Engler viscosimeter...	4	936.3	0.897	1.228	264
	10	620.6	0.893	0.809	187
	15	468.9	0.889	0.606	142
	17	391.0	0.889	0.502	130
	20	330.1	0.886	0.420	109
	25	238.3	0.883	0.295	86
	30	189.7	0.879	0.228	71
	37.8	146.2	0.874	0.1655	56
	25	142.3	0.871	0.1593	52
	25	173.4	0.894	0.2087	64
	20	82.9	0.855	0.0654	26
	15	88.0	0.858	0.0744	31
	25	77.3	0.852	0.0555	23

If it is assumed that the equation[2]

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[1] For conversion table of different units of viscosity, see Winslow H. Herschel, Bureau of Standards, *Technologic Paper* **100** (1917), 5.

[2] Winslow H. Herschel, Bureau of Standards, *Technologic Paper* **112** (1919), 19.

$$\text{Kinematic viscosity} = \frac{\text{viscosity in poises}}{\text{density in g. per cc.}} = 0.00220\,t - \frac{1.80}{t} \qquad (3)$$

(in which t is the time of discharge in seconds) applies to the Saybolt viscosimeter used in the tests of Table I, the viscosity of the six samples may be calculated for the temperatures given. This equation applies only to a Saybolt Universal Viscosimeter of standard dimensions, but it is the best available for the present purpose and has been used in calculating Fig. 1. The upper curve is from data of Table I, and the lower curve from the results of tests given in Table II.

The difference between the two curves may be attributed to differences in dimensions of the viscosimeters and to inaccuracies in adjusting the speed of the MacMichael instruments so as to give a reading of exactly 10.0° M in water.

MacMichael's method of calibration is to use "a standard testing sample of known viscosity and to assume that other readings are directly proportional in value. Through a wide range this does not seem to introduce serious errors." It is evident from Fig. 1 that this method would lead to serious error unless the calibrating liquid and the sample to be tested were not greatly different in viscosity.

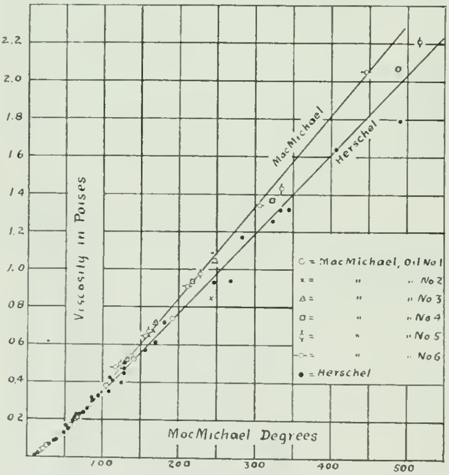

FIG. 1

The lower calibration curve of Fig. 1 is found to be represented by the equation

$$\mu = 0.00275\ (\mathrm{M} - 10)^{1.07} \qquad (4)$$

or, more simply and accurately, if only the straight part of the curve is considered

$$\mu = 0.0042\ (\mathrm{M} - 17) \qquad (5)$$

where μ is the viscosity in poises. Since Equations 4 and 5 contain two instrumental constants, two calibrating liquids (or one liquid at two temperatures) are necessary as in the case of efflux viscosimeters.

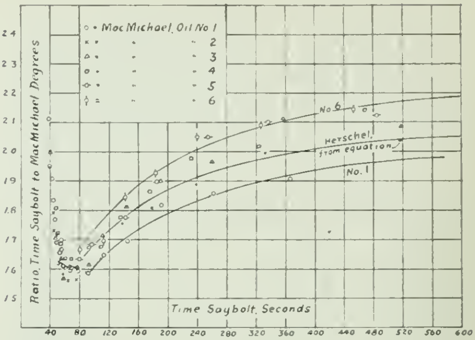

FIG. 2

From Equations 3 and 5 and the value of 0.876 for the average density of the oils at the temperature of the test,

$$t = 1.09\ (\mathrm{M} - 17)\left(1 + \sqrt{1 + \frac{688}{(\mathrm{M} - 17)^2}}\right). \qquad (6)$$

Equation 6 emphasizes the fact that the conversion formula between readings of two viscosimeters may be complex, and it is preferable to convert the readings of each instrument into poises for comparison. It also shows that a torsional and an efflux instrument cannot be compared unless the density is determined by an auxiliary instrument, since a torsional instrument measures viscosity in poises, and an efflux instrument measures kinematic viscosity.

The relation between time, Saybolt and MacMichael degrees is shown in Fig. 2, both according to Table I and to Equation 6. The ratio of t/M approaches a value of 2.18 as the viscosity increases. Figs. 1 and 2 show that Equation 5 does not apply for viscosities less than about 0.15 poise or 90 seconds, Saybolt.

THE EFFECT OF DENSITY UPON THE DEFLECTION

According to Hersey the most general equation for a torsional viscosimeter is

$$\mathrm{T} = \mu n r^3 f\left(\frac{rn^2}{g},\ \frac{r^2 n\gamma}{\mu},\ \text{shape}\right) \qquad (7)$$

where T = torque exerted on the torsional pendulum
n = revolutions in unit time
r = radius of inner cylinder
g = acceleration of gravity = 981 cm. per sec^2.
μ/γ = kinematic viscosity
f = an unknown function.

Of these three special cases considered by Hersey, the MacMichael instrument most closely approaches the second, where "the torque is not independent of the density of the sample, owing to spiral flow across the bottom or to turbulent end effects, but in which the free surface is level, so that the argument containing g in Equation 7 drops out. In this case the instrument is self-calibrating; by observing with a single liquid what function of speed the deflection is, we can at once infer what function it is of the viscosity."

In the MacMichael instrument, however, the free surface of the liquid is perceptibly parabolic, and the elevation of the surface might have a slight effect on the deflection on account of the viscous drag exerted on the tube of the pendulum. This tube is only 10 mm. ($^3/_8$ in.) in diameter where it emerges from the liquid.

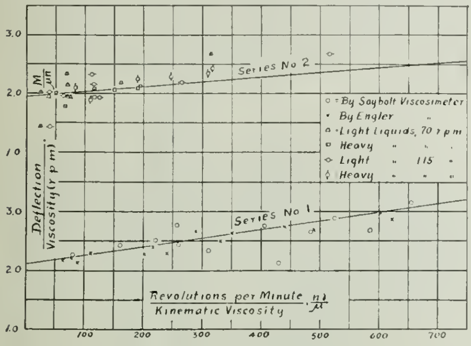

FIG. 3

Disregarding the argument containing g in Equation 7 for a given instrument it may be written

$$\frac{M}{\mu n} = f\left(\frac{n\gamma}{\mu}\right). \qquad (8)$$

Using the data of Table II, by plotting the first term against the second in Fig. 3 the equation was obtained,

$$M = 2.10\ \mu n + 0.00150\ \gamma n^2$$
$$\text{or } \mu = 0.0042\ (M - 19.5\ \gamma). \qquad (9)$$

Comparing Equations 5 and 9 it is seen that 17 is an average value of 19.5 γ.

TESTS WITH VARIABLE SPEED

If, as suggested by MacMichael, a more viscous calibrating liquid were used in place of water, the error in adjusting the speed might be greatly reduced, but the assumption of a straight line relation between MacMichael degrees and viscosities would still cause considerable error at low viscosities. If, however, the speed were reduced so as to decrease the disturbing effects of turbulence and centrifugal force, the readings would be more nearly proportional to the viscosities, as in the ideal instrument. Tests with variable speeds were made after the torsional wire had been removed for measurement and replaced. Results are shown in Fig. 4 where the numbers on the lines are values of the viscosity in poises. The speed may be varied considerably by the adjusting screw, and still further by decreasing the current to the motor. With the rheostat employed, a minimum speed of 70 revolutions per minute could be obtained, and for the few tests at lower speeds the cup was retarded by hand, taking care to keep the deflection as constant as possible.

Fig. 4 shows that at moderate speeds, with oils of not too low viscosity, the readings are approximately proportional to the speed, but with liquids heavier than water the change in deflection is greater in comparison, for a given change of speed. An exact proportionality between speed and deflection would correspond to a constant value of the ordinate of Fig. 3. In reality, as shown most clearly from the tests with heavy liquids, the ordinate increases as the speed increases. An extension of Fig. 3 to include liquids of very low viscosity shows an approximately parabolic relation between the coördinates, the curve passing through the point having an ordinate of 8.73 and abscissa of 11,300, obtained from the calibration with water.

Table III was interpolated from Fig. 4 and other tests made with variable speed. Viscosities were calculated from Equation 3.

TABLE III—TESTS OF MACMICHAEL VISCOSIMETER WITH VARIABLE SPEED

Liquid	Viscosity Poises	Density at Temperature of Test	Deflection M at Speed of 70 Rev. per Min.	85	100	115
Sucrose..........	0.479	1.285	70	90	109	129
Sucrose..........	0.603	1.293	87	111	135	158
Sucrose..........	0.796	1.303	116	147	176	206
Glycerin.........	0.437	1.207	65	85	103	122
Glycerin.........	1.298	1.229	162	203	243	282
Glycerin.........	1.698	1.234	237	295	353	410
50 per cent alcohol	0.0224	0.929	8	10	12	15
Mineral oil.......	2.710	0.923	383	465	548	630
Mineral oil.......	2.621	0.915	264	320	375	432
Mineral oil.......	1.683	0.914	230	279	328	377
Mineral oil.......	0.926	0.897	151	183	215	247
Mineral oil.......	0.879	0.887	120	145	171	196
Mineral oil.......	0.864	0.867	130	158	186	214
Mineral oil.......	0.835	0.897	113	137	161	185
Mineral oil.......	0.393	0.902	60	73	86	99
Mineral oil.......	0.203	0.909	38	47	54	62

From tests of Table III at 70 revolutions per minute, a new equation was obtained as shown in Fig. 3. This gave

$$M = 1.95\ \mu n + 0.000833\gamma n^2 \qquad (10)$$

or, with an average density of 1.04 and speed of 70 revolutions per minute,

$$\mu = 0.0073\ (M - 4.1\ \gamma) = 0.0073\ (M - 4). \quad (11)$$

The disagreement between Equations 9 and 10 may be due to the neglect of the term rn^2/g in Equation 7 as well as to the change in conditions due to removing and replacing the torsional wire. The method of fastening the wire does not permit an exact adjustment of its length.

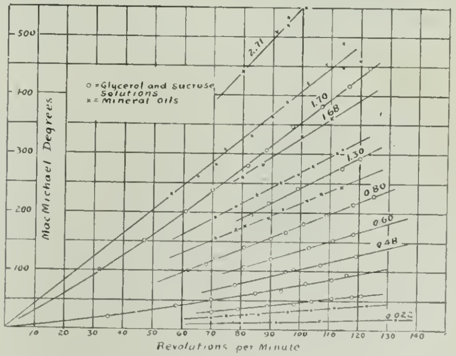

FIG. 4

Fig. 5 shows results of tests with variable speed. In the main figure the curves are calculated from Equation 10 for the average density. It will be seen that liquids with high density show in general higher deflections at the higher speeds than are given by the oils or by the curves. The curve for highest speed in Fig. 5 lies between the two curves of Fig. 1. Equation 11 and the deflection for a speed of 70 revolutions per minute were used to determine the viscosities at some of the points listed as determined by equation. These points, therefore, merely show the change of deflection with change of speed, and do not help locate the position of the curve for lowest speed.

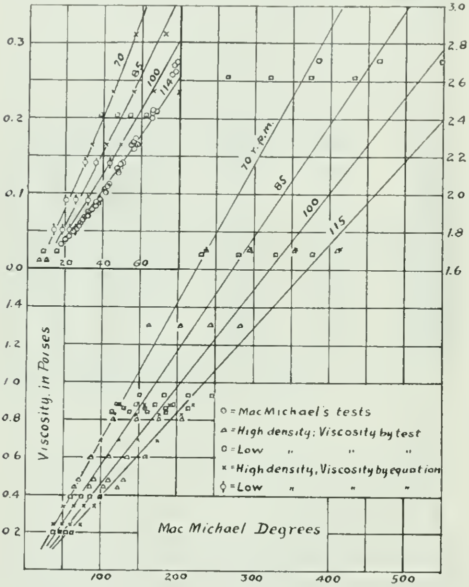

Fig. 5

For tests at very low viscosities, shown in the insert on an enlarged scale, Equation 10 does not apply. and the curves were calculated from Equation 4, assuming the deflection proportional to the speed.

METHODS OF INCREASING RANGE OF MEASURABLE VISCOSITY

Since the deflection is limited to 600° M it may be calculated from Equation 5 that the maximum viscosity which can be measured if the speed of the instrument is adjusted so as to give a deflection of 10° M with water will be about 2.45 poises. A reduction of speed to 70 revolutions per minute would increase the maximum measurable viscosity to 4.0 poises, and at the same time make the deflections at low viscosities much more nearly proportional to the viscosity.

Viscosities up to any desired magnitude could be measured by increasing the diameter of the torsional wire. There is difficulty, however, in obtaining suitable calibrating liquids for heavy wires, since the measurement of viscosities above about 20 poises by the most accurate capillary tube method is open to considerable question on account of possible drainage errors.

If the speed is reduced so that the deflection is proportional to the viscosity, then the viscosity would be proportional to d^4G with a given speed, deflection, and length of wire. The viscosity of a very viscous liquid may thus be calculated from values of d^4G for two wires, using a large wire for the liquid to be tested, and calibrating the small wire by liquids of known viscosity. The determination of diameter and torsional modulus of elasticity with sufficient accuracy is difficult, and this method should only be used when sufficiently viscous liquids for direct calibration cannot be obtained. Care should be taken not to use plastic substances[1] either as calibrating liquids or as liquids to be tested.

No definite point can be set as the minimum viscosity which can be measured with a given wire. It might, however, be pointed out that it is impracticable to make readings closer than to the nearest MacMichael degree, and that an error of 1° in a reading of 18° M (the lowest value given in the Eimer and Amend table) is an error of over 5 per cent.

There is some danger of damaging the wire when unhooking the pendulum to clean it, and this furnishes the practical limitation to the fineness of wire which can be used. There should be no difficulty in obtaining a suitable calibrating liquid, since water with a viscosity of from 0.01519 poise at 5° C. (41° F.) to 0.002992 poise at 95° C. (203° F.) may be used.

CONCLUSIONS

Every MacMichael instrument should be calibrated by the operator on account of unavoidable differences in dimensions of instruments, especially of the torsional wire. Calibration is necessary because the relation between instrumental readings and viscosity cannot be calculated from the dimensions of an instrument.

The method of calibration suggested by MacMichael, of adjusting the speed until a deflection of 10° M is obtained with water, is inadequate because adjustments cannot be made with sufficient accuracy and because there are two instrumental constants. On account of the marked effect of differences in density, two liquids (or one liquid at two temperatures) of approximately the same density as the liquid to be tested should be used. This would make it inadvisable to calibrate with sucrose solutions an instrument intended for use with oils.

This Bureau is at present prepared to certify to the viscosity of calibrating liquids having a viscosity not exceeding 20 poises. It is believed preferable for interested parties to send samples of, say, 100 cc. (4 oz.) to the Bureau for tests, rather than for the Bureau to furnish large samples in tin containers as suggested by MacMichael.

Equations showing the relation between MacMichael degrees and poises have been given. These show the general form of equation to be expected, and serve as a guide in calibrating instruments. They are not intended for use as standard equations to be applied to all MacMichael instruments with medium sized wires.

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[1] For the distinction between plastic substances and viscous liquids see E. C. Bingham, Bureau of Standards, *Scientific Paper* **278** (1916), 310.

AN ELECTRICALLY HEATED BOMB FOR AMMONIA SYNTHESIS[1]

By R. O. E. Davis and Harry Bryan

Bureau of Soils, Department of Agriculture, Washington, D. C.

Received October 2, 1919

In carrying on work on the synthesis of ammonia one of the first things necessary was to design a bomb to contain the catalyst. As the reaction $N_2 + 3H_2 = 2NH_3$ requires a catalyst working at high pressure and a fairly high temperature it was necessary for the bomb to meet some unusual conditions.

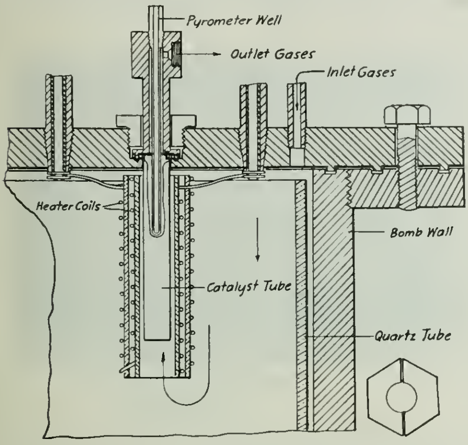

Fig. 1 Fig. 2

Fig 1—Arrangement of Bomb Head with Catalyst Tube Attached
Fig. 2—Split Nut for Holding Catalyst Tube in Position.

The type of bomb described below has been used by us in the work done in coöperation with the Nitrate Division of the War Department on the synthesis of ammonia. Several different designs were tried and most of the essentials worked out by the authors, with some modifications made with the coöperation of the Nitrate Division of the Ordnance Department. Capt. P. C. Landolt suggested a modification of the catalyst tube which resulted in the use of a flanged top, though the method of attaching and removing it is original with us.

The size used for experimental purposes will allow the use of 100 cc. of catalyst. The outer shell is made of Ni-Cr iron, regular gun steel forgings, obtained from the Washington Navy Yard. These are bored out to give a wall 1.5 in. thick. To the top of this shell screws a flange of the same material, and to this flange is bolted the plate forming the head of the bomb. The inside dimensions of the bomb here shown are 4.25 in. in diameter × 15 in. long. Closure is effected by means of recessed rings in the end of the cylinder wall, and corresponding raised rings on the cap, using a thin copper gasket between the two.

The head of the bomb carries the heater, catalyst tube, and inlet and outlet pipes. The heating is done internally by electricity. The sides of the bomb are protected by a fused quartz or glass tube. Other types of insulation proved ineffective because of the permeability to hydrogen and the high heat conductivity of hydrogen.

The heater devised after many trials is made up of two concentric alundum tubes of 1 and 2 in. internal diameter, wound in series with double strands of No. 14 nichrome wire. This will maintain a temperature within the catalyst of 550° C. The gases flowing into the top of the bomb pass down the outside of both tubes and up through a steel tube which carries the catalyst and which slips inside of the smaller alundum tube. The gases pass over the catalyst, which occupies 100 cc. volume, and out at the top of the chamber. A pyrometer well inserted through the outlet piece dips to one-third the depth of the catalyst chamber, and is believed to measure the average temperature of the catalyst. The arrangement of the head of the bomb and heater are shown in Fig. 1.

After the head has been once bolted on it is not necessary to again remove the bolts unless the heater becomes damaged in some way. The catalyst tube is made of thin steel with a flange at the top. This flange attaches to a similar flange on the outlet piece by means of small steel I-pins with a copper washer between the two flanges. The tube is made gas-tight in the head by use of a copper washer and pressed down by means of a split nut (Fig. 2). For filling, the nut is removed and the outlet piece lifted out. The catalyst tube comes with it. The inverted tube is filled from the bottom, a layer of steel wool placed on it and nichrome gauze held in place by a steel ring closes the end. A stream of dry gas is kept flowing through the bomb and the catalyst tube during all these operations.

The method of introducing the electric current to the bomb is shown in Fig. 3. This lead is about 18 in. long and is made of cold rolled steel with $^1/_2$ in. wall. The current is carried by the steel rod passing through the center but electrically insulated from the sides by means of glass. A gas-tight joint is made near the top. An enlargement on the central rod carries a fiber washer on the under side and a fiber cap on the upper. The steel cap when screwed in place forces the washers against the steel faces on the rod which carry slight grooves and a gas-tight joint is effected. The leads are made of considerable length to prevent their becoming too hot at the upper end and burning the fiber washers, thereby causing the joints to leak

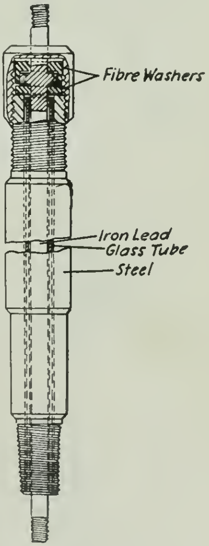

Fig. 3—Electric Lead for Introducing Current to Heater within the Bomb

gas. The steel rods are $^3/_8$ in. and attached to them are the wires by which the heater is supported.

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[1] Published by permission of Chief of Ordnance.

The heater is practically indestructible, and as it operates in a reducing atmosphere the wires can carry a considerable overload, so long as the melting point of the resistance wire is not reached.

In Fig. 1 the leads are shown in the head of the bomb. Because of the difficulty of using a wrench on the split nut with leads in this position, on one bomb they were set at an angle of 45° to the top, and on another were placed in the sides of the bomb just below the flange. All three methods were used successfully, though the last is most convenient.

A NEW TYPE OF CONDENSER FOR THE DETERMINATION OF CRUDE FIBER

By C. A. Clemens

Food and Drug Department Laboratories, State of South Dakota, Vermilion, S. D.

Received October 14, 1919

Numerous modifications of the reflux condenser for the determination of crude fiber by the official method of the Association of Official Agricultural Chemists have been suggested. The latest and best of these is the one designed by Howell D. Spears.[1]

A condenser has been designed and used in the laboratory of the South Dakota Food and Drug Department, however, which has all the advantages of the aforementioned apparatus and at the same time several additional ones.

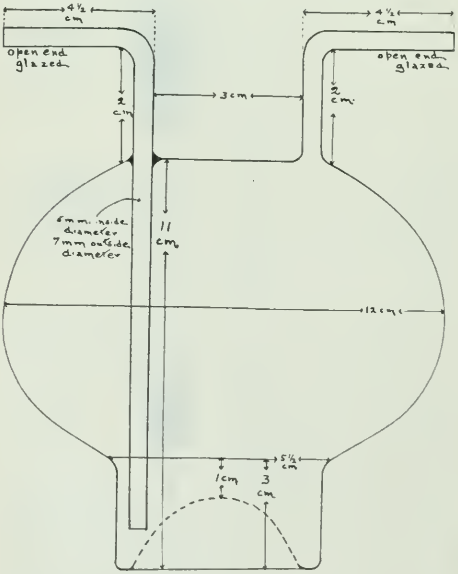

Fig. 1

The condenser (Fig. 1) consists of a glass bulb, one side of which is blown in such a manner as to extend downward. The lower surface of this projection is concave, thus the bottom is ring-shaped and furnishes a suitable surface upon which the apparatus may rest when not in use. Into the top part of the bulb two glass tubes are sealed, one serving as an inlet and the other as an outlet for a stream of cold water. The condenser is designed to rest upon a lipless beaker. Further support is furnished the condenser by attaching a wire to the inlet and outlet tubes and fastening it to an iron rod clamped to a ring stand. Supported in this manner the beakers can be removed without disturbing the condenser. Several condensers are usually arranged to form a series (Fig. 2).

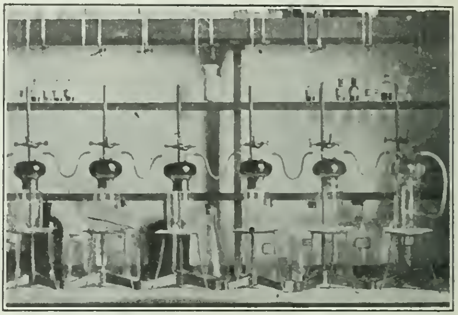

Fig. 2

This condenser has an increased surface for condensation and is constructed so that the vapors begin condensing sooner than in other forms of condensers suggested for this purpose. This reduces the loss by evaporation to a minimum. The form of the condenser is such that it also prevents foam rising to the top of the beaker. The concave surface in the projected portion of the condenser causes the condensed liquid to return by numerous routes, thus tending to break up the foam more than if it were returned at only one point. If this is insufficient to break up the foam it is immediately broken upon contact with the portion of the condenser that extends downward into the beaker, consequently there is no possibility of foaming over. The condenser can be used with lipless beakers ranging in size from 500 cc. to 1000 cc., either tall or wide form. Other advantages are its compactness, lightness, and the ease with which it is set up and taken down. The advantages of using a beaker instead of a flask are obvious. Experience has shown that condensation is practically complete when using this apparatus.

The following are some of the duplicate determinations made with this apparatus:

	Crude Fiber (Per cent)	
Linseed Oil Meal	8.11	8.20
Mixed Feed	9.53	9.60
Sugared Pig Feed	23.50	23.74
Commercial Feed	5.78	5.48
Oil Meal	7.66	7.55
Shorts	8.30	8.20
Middlings	3.10	3.07

The above determinations were made by the double filtration method. White china silk was used for the acid filtration. The silk was cut into circular pieces with a diameter of about 12.5 cm. These were folded and used in funnels in the same manner as filter papers. Alundum crucibles were used for the alkaline filtration.

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[1] This Journal, **11** (1919), 140.

The apparatus can also be used as a reflux condenser in organic preparations. Credit should also be given to Miss Vanna Elliott and Mr. Guy G. Frary for aid and helpful suggestions.

PURIFICATION OF COMPRESSED GASES IN TESTING CATALYSTS FOR AMMONIA SYNTHESIS[1]

By R. O. E. Davis

Bureau of Soils, Department of Agriculture, Washington, D. C.

Received October 2, 1919

The method of purification of gases described below is the one used in testing catalysts at the Arlington, Virginia, plant in work on the synthesis of ammonia carried on in coöperation between the Bureau of Soils, U. S. Department of Agriculture, and the Nitrate Division of the War Department. I wish to acknowledge especially the services of Captain P. E. Landolt in offering suggestions as to the arrangement and installation of the purification set.

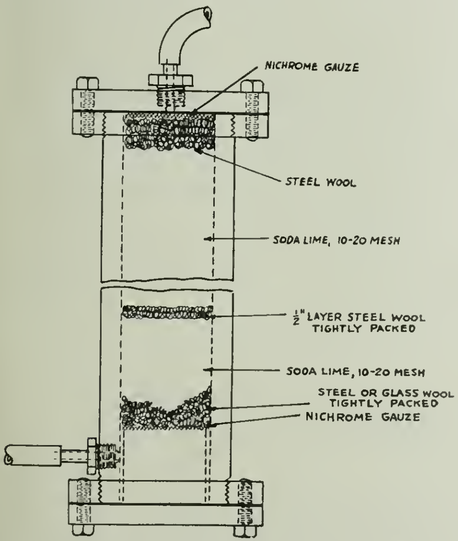

Fig. 1—Purification Chamber, Showing Connections and Manner of Packing

PREPARATION OF GAS—The gases, hydrogen and nitrogen, used for testing catalysts as to their power to act in ammonia synthesis need to be as pure as possible in order to test the catalyst under favorable conditions. The source of gas used is liquid ammonia, decomposed by iron catalyst at 675° C. This gives a fairly pure gas but impurities are sometimes present. For instance, amines are known to be present, with occasional traces of carbon monoxide and sometimes sulfur. The hydrogen and nitrogen formed by decomposition by heat still carry a small amount of ammonia and are, therefore, scrubbed with water to remove most of this and collected in a gas holder over water. The amount of ammonia in the scrubbed gas is ordinarily about 0.04 per cent.

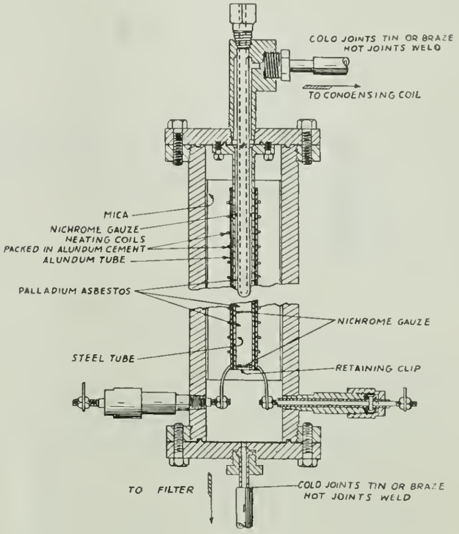
COLD JOINTS TIN OR BRAZE HOT JOINTS WELD
TO CONDENSING COIL
MICA
NICHROME GAUZE
HEATING COILS PACKED IN ALUNDUM CEMENT
ALUNDUM TUBE
PALLADIUM ASBESTOS
NICHROME GAUZE
STEEL TUBE
RETAINING CLIP
TO FILTER
COLD JOINTS TIN OR BRAZE HOT JOINTS WELD

Fig. 2—Palladium Chamber, Showing Connections, Construction of Heater, and Pyrometer Well

The gases in the gas holder in the proportion of one part of nitrogen to three of hydrogen may contain traces of CO, some CO_2, and oxygen and water vapor derived mainly from their contact with water. The presence of CO is rare. Carbon dioxide may be present but is not so undesirable as the others. Ammonia sometimes is as high as a few hundredths per cent. Oxygen is present in about 0.02 and 0.03 per cent and sometimes considerably higher. Water, of course, is present to the point of saturation at the temperature of the gases. On compression the water is partly removed, some of it condensing in the compressor cylinders, but the gases passing from the compressor at 100 atmospheres still carry water and the other impurities. Oxygen and water are both extremely poisonous to some catalysts.

PURIFICATION OF GAS—The compressed gases pass through a system of seven chambers for the removal of these impurities. These chambers are steel cylinders (Fig. 1) 24 in. long, 3$^3/_4$ in. inside diameter, with $^3/_4$ in. wall, and have flanged ends for closing. The heads are made gas-tight by use of copper gaskets, and the blind flange carries ridged rings which fit into corresponding grooves in the end of the cylinder. These cylinders have the inlets at the bottom and the outlets at the top. The system is made up of a steel wool filter for catching oil and water spray, a palladium chamber for removal of oxygen, a water trap, another steel wool filter, 2 soda lime and calcium chloride chambers, used alternately to allow refilling for removal of water and carbon dioxide and ammonia, a phosphorus pentoxide chamber and a sodamide chamber

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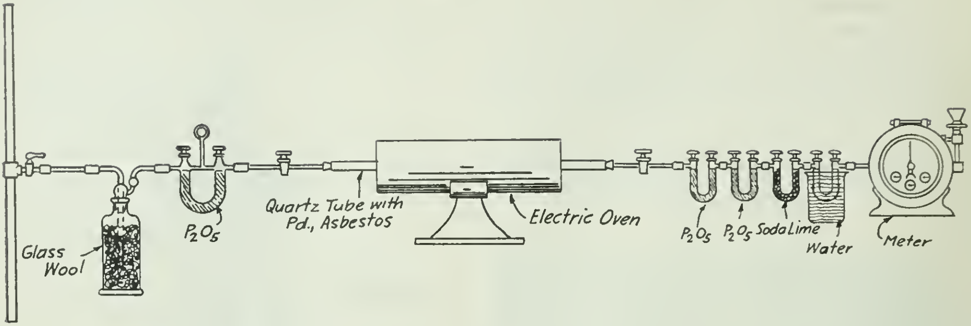

Fig. 3—Apparatus Used for Analyzing Gases for Oxygen and Moisture

or removal of final traces of moisture and carbon monoxide.

The palladium chamber is arranged differently from the others (Fig. 2) in that it is supplied with electric heat. The central steel tube attached to the head is filled with steel wool mixed with 5 per cent palladinized asbestos. This fits into an alundum tube wrapped with nichrome resistance wire. The gases enter at the top, flow over the outside of the heater and up through the central tube, coming in contact with the palladium, where the oxygen is converted to water. The temperature is maintained at 300° to 400° C. The gases are in this tube ordinarily from 12 sec. to 2 min., depending on the rate of circulation of the gases.

The sodamide chamber is heated by an external winding to slightly over 100° C. Carbon monoxide reacts with sodamide as follows:

$$2NaNH_2 + CO \longrightarrow CH_4 + Na_2O + N_2$$

and with hydrogen sulfide according to the reaction

$$2NaNH_2 + H_2S \longrightarrow Na_2S + 2NH_3$$

ANALYSIS OF GAS—After the gases pass through this train they are carried to the catalyst chambers. A valve in the gas line allows of the sampling of the gases for analysis. A slow flow of the gas, about 50 cu. ft. (Fig. 3) per day, from this valve passes through a train consisting of a glass wool filter, phosphorus pentoxide tube for removal of water, overheated palladium asbestos for removal of oxygen, through another phosphorus pentoxide tube to catch the water formed, two guard tubes of P_2O_5 and soda lime, and to a gas meter. The P_2O_5 tubes are removed and weighed every 8 hrs. and the amounts of water and oxygen in the gas determined.

At the suggestion of Capt. H. A. Curtis, the quartz tube was replaced by a glass one with the stopcocks sealed on to eliminate the danger of burning the rubber stoppers used with the quartz tube.

Percentages of oxygen and of water run in the order of 0.001 per cent and 0.0001 per cent, respectively.

ADDRESSES AND CONTRIBUTED ARTICLES

POTASSIUM NITRATE FROM THE CHILEAN NITRATE INDUSTRY

By P. F. Holstein

Assistant Administrator, Oficina Delaware, du Pont Nitrate Company, Taltal, Chile

Received October 1, 1919

Most of the information published regarding the possibilities of the production of potash in the Chilean Nitrate "Oficinas" and the present status of the question has been entirely general in character and at times misleading. The importance of this source of supply has been appreciated indeed by only very few of the nitrate producers themselves, yet during the war and at the present time several Oficinas (not more than half a dozen in all) manufactured a grade of nitrate containing a high percentage of potassium nitrate. Oficina Delaware of the du Pont Nitrate Company, a subsidiary of E. I. du Pont de Nemours and Company, has been the pioneer in this new development, which bids fair to be a factor of considerable value both to the nitrate producer and the potash consumer. The industry at the present time seems to be in rather a receptive mood as regards development of new methods, as is evidenced by numerous experimental plants, and it is very probable that the next few years will see the production of potassium nitrate in increasing quantities from the pampas of Chile. This article aims to present some of the main facts of the situation and to describe briefly the means actually at hand by which potash may be recovered.

During the year ending June 30, 1918, there were produced in Chile 64,340,267 quintals of nitrate (one quintal = 101.4 lbs.) or over six and a half billion pounds. The average potassium nitrate content of all the nitrate shipped is probably about 2 per cent, so that there were contained in this nitrate about 130,000,000 lbs. of potassium nitrate for which the producer received no additional profit. Calculated on a basis of K_2O this represents 30,000 tons of potash or about 21 per cent of the total consumption of the United States.

That this potash may be separated successfully and sold as a distinct product there is not the least doubt. This has been done since 1914 by a number of Oficinas and there are probably 100 more in the country that could do the same. Even if the price of potash should drop to the pre-war level there would still remain a substantial profit to the nitrate manufacturers, a fact of importance in meeting competition from artificial nitrate in years to come. The additional equipment necessary requires but a comparatively small outlay and should, in addition to the recovery of potash, have a definitely beneficial result on the percentage extraction of the ordinary nitrate. Moreover, this development occurs in an industry already established and accustomed to the handling and treatment of solutions on a large scale.

For many purposes there is a great advantage in the fact that this potash is in the form of nitrate, not chloride or sulfate. In this respect it differs from the potash from all other sources except the "East India Crude" product. It may be refined readily to pure potassium nitrate, or used in fertilizers. The latter is a larger and more likely field The product as turned out by the Oficinas would be a mixture of sodium and potassium nitrates containing from 20 per cent to 80 per cent of the latter salt.

The grade manufactured by any single plant depends primarily on the percentage of potash in the "caliche" or crude nitrate ore. An Oficina having 2 per cent to 3 per cent potassium nitrate in its caliche may easily recover potash in good quantity. The caliche of a majority of Oficinas will contain this amount and there are many having ore up to 5 per cent or even 7 per cent potassium nitrate. Those having a high percentage of potash in their ore have, of course, a great advantage both as to grade of product and as to cost of production. In fact, an Oficina having 5 per cent potassium nitrate in the ore may produce a certain amount of a marketable product high in potash at only a negligible cost above that of its regular sodium nitrate.

With ore of 3 per cent potassium nitrate a grade of high potash nitrate containing 25 per cent, 40 per cent, or 60 per cent may be made, depending upon the method of manufacture. An Oficina with a production of 50,000 quintals per month and an ore averaging 3 per cent potassium nitrate may divide this total production into approximately 40,000 quintals of ordinary nitrate and 10,000 quintals of "high potash" nitrate containing 25 per cent potassium nitrate, or 43,750 ordinary nitrate and 6,250 high potash nitrate containing 40 per cent potassium nitrate, etc. The production of this extra grade of nitrate will not as a rule add to the sum total in quintals of the "make" of the Oficina, but merely convert part of it into a more valuable product than ordinary Chilean nitrate.

The high potash nitrate is separated from the mother liquor resulting from the treatment of the caliche. The composition of the hot concentrated liquor that is run from the boiling tanks to the crystallizing pans varies with each plant, and from day to day at the same plant, depending upon the class of material being extracted. The two following analyses are more or less typical of Oficina Delaware, representing liquors obtained from caliches of between 2 per cent and 3 per cent of potash calculated as potassium nitrate:

	HOT LIQUOR	MOTHER LIQUOR
	(G. per 100 G. Water)	
Total Salts	146.61	90.99
Sodium Nitrate	100.04	40.95
Potassium Nitrate	20.87	19.96
Sodium Chloride	19.02	22.17
Specific Gravity	1.5050	1.4225
Temperature ° C	74	9.5

There are many other salts in solution, such as sulfates, borates, iodates, perchlorates, magnesium, calcium, etc. The analyses given, however, are sufficient for this discussion.

The hot crystallizing liquor stands from 5 to 10 days in the crystallizing pans during which time there is considerable air evaporation. This accounts for the fact that the weight of sodium chloride per 100 g. water has increased. For the same reason it will be evident that a small amount of potassium nitrate has deposited along with the sodium nitrate.

The important point is that the mother liquor is saturated at air temperature with potassium nitrate in a solution of many other salts. Very often the solution is saturated with potassium nitrate at temperatures much above that of the air, in fact, as high in some Oficinas as 40° C. Under these conditions there will be deposited along with the sodium nitrate, on cooling, from 1 per cent to 10 per cent of potassium nitrate, and even more in a few plants exceptionally fortunate in the potash content of their ores. As the mother liquor is used over and over again in the extraction of fresh lots of ore it takes up more potash, depositing it in turn in the nitrate, except in cases where the potash is recovered and removed from the mother liquor before returning it to the plant. Referring to the above analyses it will be seen that if the hot liquor had contained 35 g. of potassium nitrate per 100 g. of water there would have been deposited about 15 g. when the liquor had cooled. As about 60 g. of sodium nitrate deposited, and the final product after deducting moisture, salt, insoluble matter, and sulfate is about 95 per cent nitrates, it is clear that the deposit would have contained about 19 per cent potassium nitrate. If the hot liquor had contained 25 g. potassium nitrate per 100 g. of water the deposit would have contained something over 7 per cent potassium nitrate.

This is exactly what occurs in the majority of Oficinas. The mother liquor, being used repeatedly through the boiling tanks for the extraction of fresh caliche, becomes rich in potash. The hot liquor as run to the crystallizing pans will not be saturated with potash, but on cooling will be saturated with this salt at a temperature above that of the final temperature to which the liquor cools. Hence the 1 per cent to 10 per cent of potassium nitrate contained in the product shipped from the Oficinas and sold as Chilean nitrate.

FRACTIONAL CRYSTALLIZATION—This suggests the first, simplest and cheapest means by which a nitrate containing a high percentage of potassium nitrate may be manufactured, available on any considerable scale, however, only for those Oficinas having a fairly high percentage of potash in their ores, close to 5 per cent calculated as potassium nitrate. Fractional crystallization will then give a commercially profitable high potash nitrate at an insignificant cost above that of their regular nitrate. The liquor when it has reached the proper temperature in the crystallizing pans is merely transferred to other pans where it cools to air temperature, this second deposit being the high potash nitrate. This method does not recover much of the potash in the ore, but does have the advantage of extreme cheapness and ease of operation and might be used immediately by a number of Oficinas which hesitate to install an expensive system. As long ago as 1912, Oficina Delaware recovered a small quantity of high potash nitrate regularly by this method, and one other company at least, to the writer's knowledge, recovered a certain amount by separating the crystals on top in the crystallizing pans. During the war several plants in Tarapacá produced high potash nitrate by fractional crystallization and are continuing to do so. There are undoubtedly many Oficinas which could make a certain quantity of high potash nitrate by this means, but are deterred, either by ignorance of the facts or by lack of a technical staff.

The fact that the mother liquor is saturated with respect to potassium nitrate, or at least contains a fair amount, gives two other methods by which it may be recovered, *i. e.*, evaporation or refrigeration.

EVAPORATION—By evaporation of the mother liquor there will result a solution concentrated in nitrate, and more or less of the character of the hot crystallizing liquor which is run from the boiling tanks, with the difference that the concentration of potassium nitrate is greater. As the solubility of sodium chloride in a nitrate solution is somewhat less at higher temperatures than in a cold solution, this salt is deposited during the evaporation. There is also, of course, a concentration of various impurities, magnesium salts, boric acid, iodates, etc. Fig. 1 gives cooling curves for a solution prepared by the evaporation of mother liquor. It will be observed that some boric acid is deposited, the nitrate manufactured by this method usually containing about 3 per cent. In operating practice it is usually better to return the mother liquor resulting from the evaporated liquor to the boiling tanks instead of mixing it with the regular mother liquor for evaporation. The liquors are thus "cleaned" of impurities by passing through the boiling tanks over fresh ore. It is also wise to regulate carefully the time of standing in the crystallizing pans, as otherwise the nitrate will be rather high in sulfate and magnesium, and, therefore, in moisture.

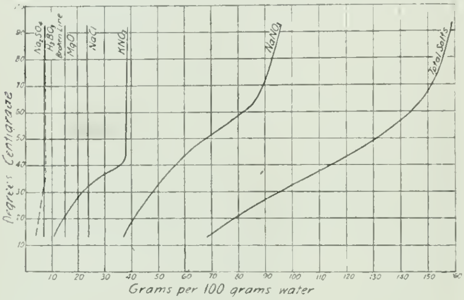

FIG. 1

Little difficulty will be encountered, however, in producing a product containing 93 per cent to 95 per cent total nitrates, depending of course upon the potash content of the mother liquor evaporated. Oficina Delaware regularly produced a product by this method containing from 25 per cent to 30 per cent potassium nitrate, and several other Oficinas, having more potash in their ore, a higher grade.

It will be evident from the cooling curves that an evaporated liquor may be fractionated to give a fraction high in potash and a fraction relatively low. There is more or less difficulty in reducing the potash content of the first fraction low enough to avoid a large loss of potash, and unless there is an additional premium for the higher grade material that thus may be separated it is not advisable.

REFRIGERATION—The third method for the manufacture of high potash nitrate, *i. e.*, refrigeration of the mother liquor, has been in operation in Oficina Delaware since November 1918, having superseded evaporation. This process is based upon the fact that the mother liquor is saturated with potassium nitrate at air temperature and that at lower temperature the solubility of potassium nitrate decreases more rapidly than the solubility of sodium nitrate. For instance, at 20° C. in the mother liquor there are approximately 55 g. of sodium nitrate and 25 g. of potassium nitrate per 100 g. water; at a temperature of —10° C. there are approximately 35 g. of sodium nitrate and 10 g. of potassium nitrate per 100 g. water, or in cooling through this range of temperature something over one-third of the sodium nitrate is deposited and nearly two-thirds of the potassium nitrate. In this particular instance 20 g. of sodium nitrate would be deposited and 15 g. of potassium nitrate. Assuming the product to be 95 per cent nitrates, the mixture would contain 40 per cent potassium nitrate. The mother liquor which gives a 25 to 30 per cent product by evaporation without fractional crystallization will give by refrigeration a product containing 40 per cent potassium nitrate.

Fig. 2 gives cooling curves for a certain mother liquor from 14° C. to —10° C. One of the main points to be observed is that no boric acid, magnesium salts, or chloride is deposited, and that sulfate did not precipitate until temperatures under —5° C. are reached. This is found to be true in practice, giving a much purer product than is obtained by evaporation. Below are given typical analyses of nitrate made by the two processes:

HIGH POTASH NITRATE

	Manufactured by Evaporation Per cent	Manufactured by Refrigeration Per cent
Moisture	3.72	0.79
Insoluble	0.10	0.09
NaCl	0.76	0.56
Na_2SO_4	0.44	0.35
Nitrate (by difference)	94.98	98.21
CaO	0.16	0.04
MgO	0.44	0.20
$KClO_4$	0.55	0.30
H_3BO_3	3.00	0.17
KNO_3	28.07	42.00

The greatest difference in the impurities is that of the boric acid, a fact that is of importance if the nitrate is to be refined for the manufacture of pure potassium nitrate.

By the addition of a small quantity of water to the mother liquor before refrigeration a nitrate very much higher in potash (60 to 85 per cent) can be produced in a single operation. This involves a great economy in case the nitrate is subsequently to be refined.

Exactly the same recovery of the potash, between 30 and 60 per cent, in the ore will be obtained by either evaporation or refrigeration. It is not entirely clear why more of the potash in the ore does not pass into solution, but the probabilities are that it is because it occurs in the caliche in the form of sulfate or difficulty soluble double sulfates or double salts. Some work has been done upon this subject with the hope of increasing the recovery and it is not improbable that a recovery may be obtained as good as that upon the total nitrate. The ordinary Oficina throws away daily in the tailings about 25,000 lbs. of potassium nitrate. Its recovery commercially is not, however, as simple as would appear at first thought.

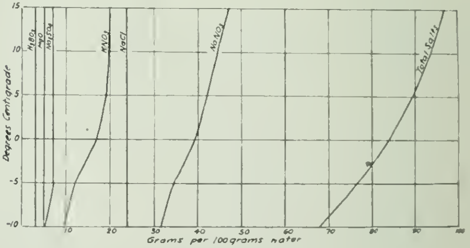

FIG. 2

Whichever method for the recovery of potash an Oficina may choose, fractional crystallization, evaporation, or refrigeration, will depend a great deal upon their present plant installation and method of operation, and the conditions peculiar to their own particular plant. The character of the ore and its potash content, the air temperature in summer and winter, the composition of the mother liquor, and numerous other factors must all be given consideration. Refrigeration will produce a higher grade nitrate at a much lower cost than will evaporation. On the other hand, evaporation, if properly carried out in the right type of evaporator, has the advantage that the water removed from the system may be used as additional wash water for washing the tailings in the boiling tanks, thus increasing the recovery of sodium nitrate. The usual type of evaporator will not be found satisfactory because of the heavy precipitation of salts during evaporation. The tubes must be cleaned by washing and if the design of the evaporator makes necessary a large quantity of water for this purpose, considerable of the advantage that otherwise would be gained by driving off water from the system will be lost. Each Oficina should have its own solution as to which method will give the cheapest cost and the best results.

In the above brief discussion only those methods have been mentioned which have been tried on an actual operating scale. There are a number of other possible means, but the ones described are those which at the present time are giving satisfactory results in the few Oficinas that so far have appreciated the opportunity that they have for the manufacture of a valuable by-product. A number of the larger companies are giving serious study and consideration to this new development of the nitrate industry and a year undoubtedly will see a number of other Oficinas producing potash.

UTILIZATION OF THE SHARK FOR FOOD AND LEATHER[1]

By Allen Rogers

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From time immemorial the shark has been considered as an enemy to man and as a scavenger of the sea. He has been pictured as the cannibal of the deep, and in fiction has been painted as the monster who lurks about the ill-fated ship in order to devour the unfortunates who may have met their death in the gale or on the reef. We, therefore, for generations have cherished an antipathy for this creature of the sea and have been very willing to accept as fact all of these stories, never stopping to consider that perhaps after all the shark might have a few points in his favor.

To begin with, the shark does not live exclusively on the flesh of man. In fact, there are only a few species who would eat human flesh even if it were possible for them to secure it. The principal species considered a man eater, the tiger shark, probably has seldom had the pleasure of this delicacy. Sharks, like all other fish, live on the smaller fish; thus upholding the proverb that the big fish eat the little ones.

Sharks travel in schools or singly and are found most abundant where food fish are plentiful. They are especially fond of the mullet, menhaden, mackerel, and sea trout. Thus it will be seen that they are migratory and at various seasons are found in different waters. They are naturally warm water fish which accounts for the large number found in the Gulf of Mexico, along the coast of Florida, and the West Indies. Being rapid and powerful swimmers they often follow ships for hundreds of miles picking up food as it is thrown over the side of the vessel. Thus their diet at such times is not unlike that of our domestic hog and poultry. It is claimed by fisher folk that the shark will not eat unsound food, which shows him even more particular than our friend the porker. Why, then, if he is so clean in his habits of life should we discriminate against him?

The Bureau of Fisheries for several years has endeavored to interest the people of this country in using shark meat as an edible product, with a certain amount of success. In fact, that species of shark known as dog fish is being canned in large quantities and sold under the name of gray fish. Certain fisheries on the New England coast are removing the head, tail and fins and selling the product in Boston and New York as deep sea sword fish. In Boston also shark meat is being sold as such to the Italian trade who appreciate its food value and enjoy its delicate flavor. Why, then, should we not take a lesson from the Italians and acquire the sharkeating habit?

For the past five or six years the writer has been interested in developing a method for converting shark skins into a merchantable leather. As a result of this work several processes have been devised which have been assigned to the Ocean Leather Company operating fisheries at Morehead City, N. C., and Fort Myers, Fla. This concern alone expects to get up to a catch of 1000 fish daily, although at present they are not taking this number. The skins are now being manufactured into leather, the livers rendered for their oil, and the flesh converted into fertilizer stock. It is estimated also that at least 1000 sharks can be secured daily from the fishermen handling food fish, who at present simply kill the sharks getting into their nets and throw them back into the water. By this wasteful procedure on the part of the fishermen at least 1000 sharks daily are destroyed along the Atlantic coast. Thus not only is the skin lost to the leather trade, not only is the liver oil discarded, not only is a large amount of fertilizer material made unavailable, but at least 50 per cent of the weight of the shark which would be fit for human consumption goes to waste.

A conservative estimate based on the above figures indicates that for a catch of 2000 sharks daily, at an average weight of 200 lbs., there would be 400,000 lbs. of fish. As at least 50 per cent could be used for human consumption we would have 200,000 lbs. daily or 73,000,000 lbs. annually. Assuming that the market price could be set at 10 cents we have a saving of $7,300,000.

The question of supply is one that is constantly being asked. From personal observations and those of men who are most familiar with the subject, it seems evident that the supply is inexhaustible. Another question is often raised as to the best method to prepare the flesh for market. The answer is, cold storage. This method, however, may not always be practical in isolated fishing stations; recourse must then be made to salting, smoking, or drying. The fresh meat, however, is the most delicious, and when boiled, broiled, or baked furnishes a white, flaky food closely resembling halibut or sword fish.

A source of food supply so extensive warrants our most careful consideration and it is hoped that the time is not far off when we may overcome our prejudice and take advantage of Nature's abundant supply.

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[1] Presented before the Division of Agricultural and Food Chemistry at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 4, 1919.

NOTES AND CORRESPONDENCE

CHLORINE AND INFLUENZA[1]

By Charles Baskerville

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The sharp contrast in the number of cases of influenza during the severe epidemic of 1918, observed at Edgewood Arsenal among the soldiers on duty in the chlorine plants to others in the Chemical Warfare Service on the reservation, prompted an investigation as to experience elsewhere. Colonel Walker suspected chlorine as the benign prophylactic and Major Vaughan supported it for the writer with a detailed repor on the conditions which obtained at Edgewood. Information was then sought and secured from practically all chlorine producers in the United States and many users. No data were obtained from bleacheries (cloth) or water purification plants where chlorine was used. Cordial and frank responses came, with permission to use names in some instances. In case of others confidence was enjoined, hence with the single official reference cited, names and places are omitted in this report.

A digest of correspondence with some 25 producers of chlorine products indicates a very pronounced belief on the part of the majority that the presence of small amounts of chlorine in the air has a decided prophylactic effect in the case of influenza, or that it at least tends to minimize the severity of attacks of the disease.

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[1] Presented in abstract at the 57th Meeting of the American Chemical Society, Buffalo, N. Y., April 7 to 11, 1919.

As a result of their experience, 13 concerns considered that employees working in parts of their plants where small amounts of chlorine were apt to be present in the air are much less apt to contract the disease than are other workers. In some instances where careful records were available, there was either an entire lack of infection, or, where there were any cases of the disease, they were very light and followed by complete recovery. Some of these latter cases could be traced to exposure to infection at home or away from the works. A few instances are cited as illustrative.

In one instance, a plant located in a town where the epidemic of 1918 is reported to have raged harder than in any other town in the United States, there were very few cases in the chlorine department as compared with the rest of the plant.

A plant, in which 15 per cent of its employees were infected, reported no cases in its chemical building where chlorine was produced, nor did any occur in its bleach room.

Out of a plant force of 60, at a hydro-electric factory, there were 3 cases, 2 being men who seldom worked where chlorine was present. Out of the office force at this same establishment, there were 4 cases out of 12 employees.

At one of the government arsenals where chlorine was produced, despite the prevalence of influenza on the reservation, only one man in the chlorine department contracted it, although on account of a shortage of nurses, chlorine operators were used in this capacity.

In one plant 75 per cent of the employees (150 out of 200) had influenza. Of these, however, only one died, and there were only two or three severe cases.

Of the 12 other concerns with whom correspondence was carried on, the majority either lacked records upon which an opinion could be based, or were undecided as to the effect of chlorine as a prophylactic for influenza. Many of them expressed the opinion that chlorine workers were noticeably free from colds and other pneumatic diseases.

In one instance a decidedly negative report was given. It was believed that rather than having any prophylactic effect, it instead created a decided predisposition towards the contraction of influenza. This plant employed 1,000, 65 being girls, all the latter attending electrolytic cells for the production of chlorine. Air in the cell room averaged 0.0009 chlorine. About once a year a complete bank of cells explodes, when the chlorine rises as high as 60.36. On such occasions escapes are used and repairs made by workmen wearing trench masks. At the height of the epidemic 297 men and 31 women had the "flu," but all recovered and showed no ill after-effects.

In another plant during the first epidemic, the workers were practically exempt, but during the second, the plant was nearly put out of business for a month on account of the number of employees down with the disease.

The data may be far too few to warrant drawing any conclusion, but these facts speak for themselves. The medical profession confesses inadequate knowledge as to the etiology of influenza (or whatever it may be called), and it would be presumptuous for chemists to state that extremely dilute chlorinated air is a general prophylactic, but a chemist may repeat the words of a distinguished past president of our Society to the medical man, "Try it." It can do no harm. We got modern inhalation anesthesia and gaseous disinfection from the pneumatic era at the close of the 18th Century, so perhaps in seeking to correct unmistakable injury due to our fumes and noxious vapors, we may find that they do good when properly regulated.

A BEQUEST TO THE AMERICAN CHEMICAL SOCIETY

An important communication has just reached the offices of This Journal concerning a bequest recently made to the American Chemical Society by a prominent citizen. On request no names are mentioned in connection with the matter, but the following extract from the will is printed, not only as a matter of interest to all members of the Society, but in the hope that the example thus set may be the forerunner of many similar bequests whose cumulative effect will be the provision of a large endowment fund for problems of research and the training of research chemists. The care and thoroughness shown in drawing up the details of the will and the confidence shown in the ability of the officers of the American Chemical Society to wisely administer such a fund point the way for similar gifts in the future.—[Editor.]

......to convey, transfer, and pay all the rest, residue, and remainder of said trust fund, both real and personal, and wherever situate, to the American Chemical Society to be held by said Society IN TRUST as a separate fund, to be managed, used and expended by said Society as follows:

It is my desire and purpose that the fund be used for the encouragement and promotion of scientific and industrial research in chemistry, preferably in the United States, and that the fund be so administered as to provide for young men and women of demonstrated and exceptional capacity for chemical research, an opportunity for early recognition.

To this end I direct that the fund be held, managed, and invested by the American Chemical Society, and administered by the Directors of said Society.

Until such time as the annual income of the fund shall reach the sum of Twenty Thousand Dollars, one-half of the income shall be added to the principal of the fund, and in case of subsequent impairment of the fund, or diminution of the income therefrom, one-half of the income shall be similarly added to the principal until the annual income is restored to Twenty Thousand Dollars.

Until the annual income reaches the sum of Twenty Thousand Dollars, one-half of the income shall be devoted to the ultimate purposes of the fund, as follows:

From that half of the income available as aforesaid, there shall be set aside annually such sum as may be necessary to cover the cost of a gold medal and a bronze replica of the same to be awarded on the conditions and in the manner hereinafter provided.

The remainder of the available half of the income shall be divided annually into two or more research fellowships of equal amount, and these fellowships shall be awarded as follows:

The award shall be made by a committee of the American Chemical Society, consisting of seven members, selected annually by the Council of the Society from the membership of the Council. The first committee selected shall consist of three members who shall serve for one year, and four members who shall serve for two years, and thereafter the places of retiring members shall be filled annually by members who shall serve for two years. Not more than three members of the committee shall be members of the instructing staffs of educational institutions; and no members shall be eligible for more than two consecutive years of service If a committee having the qualifications above set forth cannot be obtained from the membership of the Council, the Council of the Society shall have the right to select such members as may be necessary from outside the membership of the Council.

Candidates for the fellowships shall be required to submit to the committee at such time and place as may be designated by the committee, a thesis embodying the results of research conducted by the candidate, together with a written statement covering the candidate's training and experience in research, with such other information as the committee may require; and shall also submit an explicit statement of plans for continuing research under the fellowship. In selecting candidates, preference shall be given to those under twenty-five years of age, unless regularly enrolled in a college, university, or technical school of recognized standing.

The committee shall, thereupon, select from among the candidates complying with these requirements, the two, who, in the opinion of a majority of the committee are best qualified to utilize the fellowships effectively in self-development as research chemists; and shall award to each of them one of said fellowships. A fellowship thus awarded shall be held for a period of two years, unless the committee for cause decides at the end of the first year that it shall not be continued. A fellowship thus discontinued may be awarded to another candidate for the succeeding two years.

The award of a fellowship shall carry the condition that the successful candidate agrees to devote substantially all of his time during the two years following the award to the prosecution of chemical research along the lines previously indicated by him, or along such lines as may at his request be later substituted therefor by the committee.

The candidate shall be further required to make to the committee reports of progress at intervals of six months, and to submit to the committee at the conclusion of the two-year period covered by the fellowship awarded to him a thesis embodying the methods and results of his research.

In case the thesis thus submitted shall embody, in the opinion of the committee, an exceptionally notable or meritorious contribution to chemical science or technology, or otherwise give satisfactory evidence of unusual research ability, the committee may award to the holder of the fellowship, a gold medal and bronze replica of the same as hereinbefore provided, such award being made publicly at such time and place as the Council of the SOCIETY may determine.

When the annual income of the fund shall have reached the sum of Twenty Thousand Dollars, continuing provision shall be made for meeting the cost of the gold medal and bronze replica which may be awarded annually, and the remainder of the income shall be divided into equal portions or fellowships, each of an amount sufficient in the judgment of the committee to provide for the expenses of an average research student for a period of one year, preferably in the United States. Thereafter, except at such times as the annual income of the fund may fall below Twenty Thousand Dollars, the committee shall award, provided a sufficient number of duly qualified candidates present themselves, as many fellowships as the income thus divided will maintain, each fellowship to be held for a period of two years unless the committee for cause decides at the end of the first year that any fellowship shall not be continued. A fellowship thus discontinued may be awarded to another candidate for the succeeding two years. The gold medal and bronze replica aforesaid may be awarded to the author of that thesis submitted by the holders of current fellowships which best meets the requirements previously set forth as constituting the basis of such award.

All unexpended balances of income at the end of every year shall be added to the principal of the fund.

In case at any time the AMERICAN CHEMICAL SOCIETY shall cease to exist or be unable for any reason to accept or carry on the administration of the trust hereby created, I nominate and appoint the National Academy of Sciences, now having its principal office at Washington, D. C., to be trustee hereunder in place of the AMERICAN CHEMICAL SOCIETY, and if the National Academy of Sciences shall decline to accept said trust, I request that the Judge of Probate having jurisdiction of this will appoint as trustee in place of the AMERICAN CHEMICAL SOCIETY, such organization, society, or institution as may be nominated by the governing board or body of the said National Academy of Sciences. Upon the appointment of any trustee to succeed the AMERICAN CHEMICAL SOCIETY, the fund shall be administered by such succeeding trustee as nearly as possible in the manner hereinbefore set forth.

It is my hope and desire that as time goes on, others, perhaps more especially those who have themselves benefited by this endowment, appreciating its value to the progress of science and industry, may be induced to add to the principal of this fund, and I suggest that this clause of my will be brought to the attention of all holders of fellowships hereunder.

CHEMICAL AND ENGINEERING LABORATORIES

During the war industrial research in the United States was greatly stimulated and the importance of the industrial research laboratory as a factor in maintaining the supremacy of an industry was more clearly recognized than ever before. As a result of this, new laboratories will undoubtedly be built and many old ones will be reorganized that they may render more efficient service.

In order that the experience of others may be available to those who are contemplating the establishment or the reorganization of their laboratories, the following list of references has been collected. With a few exceptions, only those laboratories have been included, the description of which is accompanied by drawings, plans, or photographs showing the general arrangement of the buildings or rooms. A few general references on the value of industrial research are also given.

GENERAL

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CLARENCE J. WEST

INFORMATION DEPARTMENT, ARTHUR D. LITTLE, INC.
CAMBRIDGE, MASS.

PURIFIED CRESOL (CRESYLIC ACID)

Editor of the Journal of Industrial and Engineering Chemistry:

The following comments on "Purified Cresol," by H. C. Hamilton [THIS JOURNAL, 12 (1920), 50], may be of interest.

The author states that the "three cresols are identical in composition, but have different physical and bactericidal properties"—which has, of course, long been recognized as true—but goes on, "These differences, however, are unimportant and nothing of practical value results from their separation," thereby running counter to the experience of most chemists who have handled these products, and counter to the U. S. Pharmacopoeia. *Ortho*-cresol has a markedly different (sharper) odor from the others, is more toxic, and has a coefficient only a little better than phenol itself. Even if pure isomers are too costly to produce in large quantity, a good technical "*meta-para*," approaching the U. S. P. grade or even closer boiling, is preferable to a "trikresol" containing the isomers as they come.

As to the coloring of cresol, the author states, "Sufficient observations have not been made to arrive at a theory as to the cause or causes of the change and no method has consistently prevented its recurrence." In my experience, exclusion of air and light is not enough, but if the freshly distilled sample is taken off between such limits that *all* water has previously gone over and traces of decomposition products due to excessive or too rapid heating are not yet formed, then the sample will keep colorless indefinitely. Care should be taken to prevent contamination with water vapor or droplets when condensing (take directly from distilling flask's neck, without condenser, after carefully wiping thermometer and inside top of flask); and it is best to use a glass-stoppered bottle of chemical glass, filled to the stopper, without air bubbles, and wrapped in dark paper.

I have seen a "*meta-para* cresol" that was still quite colorless after having been barreled in England, imported, and having lain in the original barrel several weeks on this side. It proved on analysis to be *free from water*. This seems to be most important; next in order are *freedom from impurities* (anything except xylenol), *light*, and last of all *air*.

RIVERSIDE, CALIFORNIA
January 10, 1920

EVERETT M. YORK

ALKALI FUSIONS. I—THE FUSION OF SODIUM *p*-CYMENE SULFONATE WITH SODIUM HYDROXIDE FOR THE PRODUCTION OF CARVACROL

Editor of the Journal of Industrial and Engineering Chemistry:

In an article of the above title in the February number of THIS JOURNAL, Gibbs and Phillips have criticized adversely the use of an atmospheric pressure type of fusion apparatus for the manufacture of carvacrol previously suggested[1] by the present authors, and instead advocate the use of autoclaves of a type to stand high pressures. Using very carefully purified chemicals and starting from sodium cymene sulfonate they quote as their highest yield one of 74.7 per cent (0.5 oz.) of the theoretical. If this were corrected for the customary loss in passing from cymene to sodium cymene sulfonate it would probably be fully 5 per cent less. During the past year, under the direction of one of us, students in chemical engineering at Columbia University have been carrying out as a class experiment the preparation of carvacrol by the method of fusion at atmospheric pressure. Better yields are now obtained than we previously quoted, as might be expected with increased familiarity with the process, *e. g.*, a distilled carvacrol yield of 76 per cent (16 lbs.) based on the cymene taken (not the intermediate sodium cymene sulfonate). This includes no allowance for the cymene set free during the fusion reaction, a product lost by the process, unless modified, advocated by Gibbs and Phillips.

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[1] THIS JOURNAL, **10** (1918), 982.

In other words we still believe the evidence strongly favors the relatively inexpensive, large capacity, covered fusion kettle working at atmospheric pressure as a manufacturing unit over autoclaves with their troubles due to high pressure, leaks, small capacity, and difficulties of even heating and agitation. However, we do wish to compliment Messrs. Gibbs and Phillips on the ingenious design of their apparatus permitting for experiments of a few grams exact temperature control, stirring, high pressure, and the handling of six fusions simultaneously.

We note with pleasure that Gibbs and Phillips confirm our small scale results that the amount of caustic "could be reduced almost to the theoretic amount required without much effect upon the carvacrol yields."[1] In experiments of plant type we found a slight increase of proportion of caustic soda desirable.

In closing we wish to call attention to the fact that some thymol is formed simultaneously along with the carvacrol. Mr. Allan Leerburger, working on a related problem with one of us, has shown that the carvacrol made from cymene by the process under discussion carries from 6 to 8 per cent of thymol. This would not be detected by the method of analysis[2] used by Gibbs and Phillips.

Arthur W. Hixson and Ralph H. McKee

Department of Chemical Engineering
Columbia University, New York, N. Y.
February 6, 1920

THE CHEMICAL FOUNDATION, INC., PATENTS[3]

Answering an inquiry from Mr. Thomas C. Dawson of the Electric Boat Company, as to the *validity of the title* of The Chemical Foundation to its patents, Mr. Ramsay Hoguet, patent counsel to The Chemical Foundation, has written the following letter to Mr. Dawson:

January 15, 1920

Mr. Thomas C. Dawson,
Electric Boat Company,
11 Pine Street, New York.

My Dear Mr. Dawson:

Answering your recent inquiry and in connection with the suggestion which has been made to you that a doubt has been raised (presumably by interested persons) as to the validity of the title of The Chemical Foundation to its patents, I submit the following:

The title of The Chemical Foundation to its patents is the same title that the purchasers of other forms of personal property from the Alien Property Custodian, such as the stock of corporations, for instance, have to the property they purchased. The Chemical Foundation obtained its patents by virtue of a sale under the Trading with the Enemy Act, and to determine the question of its title it is simply necessary to see whether the Act authorized such a sale and whether the formalities prescribed by the Act for such a sale have been complied with.

The Trading with the Enemy Act originally conferred upon the Alien Property Custodian only the power to hold as a trustee and to sell in order to prevent waste; but subsequently the Act was amended to give the Alien Property Custodian all of the rights or powers which are appurtenant to the ownership of the property "in like manner as though he were the absolute owner thereof," including the right to sell the property. Such sales (Section 12 of the Act) are required to be made at public auction after advertisement, unless the President in an executive order in which he states his reasons therefor shall otherwise direct.

That the term "property" as used in the Act includes patents and similar intangibles such as were sold to The Chemical Foundation is clear from Section 7(c) of the Act as amended, which specifically includes "patents, copyrights, applications therefor and rights to apply for the same, trademarks" within the definition of property which is subject to the Act. It is, therefore, apparent that the patents, trademarks and copyrights sold to The Chemical Foundation might be sold to it and that The Foundation would obtain a good title thereto provided the requisites of the Act were complied with.

Let me give you a short resumé of what was actually done in the case of each patent and point out to you how this complies with the provisions of the Trading with the Enemy Act.

A thorough examination of each patent title was made and a report based upon such examination was rendered to the Alien Property Custodian of the enemy ownership of each of the patents investigated. The Alien Property Custodian was thus informed of the fact of enemy ownership and the provisions of Section 7(c) requiring an investigation by the Custodian are complied with. The Custodian then issued a requirement or instrument of seizure under the provisions of Section 7(c), which seizure was served upon all persons who were known to have any connection with the property seized and was recorded in the United States Patent Office. The recording of the instrument of seizure in the Patent Office has the "same force and effect as a duly executed conveyance, transfer or assignment to the Alien Property Custodian so filed and recorded" (Section 7(c) as amended). It will, therefore, be seen that the Alien Property Custodian was properly vested with the patents under the provisions of the Act.

As to the sale, executive orders were made on February 26, 1919, and April 5, 1919, authorizing the Alien Property Custodian to sell upon such terms as he determined, the patent, trademark and copyright property thus seized; and in pursuance of such executive orders a sale was made to The Chemical Foundation and an assignment reciting the executive orders and other proceedings was executed by him on the 10th of April 1919. It is, therefore, evident that all of the statutory requirements concerning seizure and sale were complied with and the title vested in The Chemical Foundation is absolute under the Act.

Congress recognized that it must give to the purchasers from the Alien Property Custodian an absolute title and, therefore, Section 12 of the Act specifically limits any claim to any property sold, to the *proceeds of the sale* and thus prevents a recovery of the property itself. It states "the sole relief and remedy of any person having any claim to any * * * property * * * conveyed * * * to the Alien Property Custodian * * * in the event of sale or other disposition of such property by the Alien Property Custodian shall be limited to and enforced against the net proceeds received therefrom * * *."

As to the operation of the Peace Treaty, the Peace Treaty is unnecessary to validate the title of The Chemical Foundation, since, as I have pointed out above, this title is a valid title. It simply ratifies and confirms the title of The Chemical Foundation and cuts off any possible suits. Thus, Article 297 of the Treaty ratifies every action taken by the Alien Property Custodian and Annex 15 of this article makes it apply specifically to patents and similar property. This article particularly mentions the ratification of sales of enemy property under war legislation and Article 306, which relates to the re-establishment of the International Conventions relating to industrial property, specifically excepts property dealt with under war legislation, as by the Alien Property Custodian.

It seems to me inconceivable that any question should be raised as to the validity of the title of The Chemical Foundation to its patents, if it were understood that this title rests upon the same basis as the title to half a billion dollars worth of property or more, which has been sold by the Alien Property Custodian to American purchasers. There is no essential difference between patents and the stocks of corporations which have been sold to American purchasers by the Alien Property Custodian to such a great extent.

The question of the validity of the title of The Chemical Foundation to its patents has been examined independently by a number of attorneys representing important interests and they have uniformly arrived at the conclusions which I express above. I refer by permission, to Messrs. Kalish & Kalish, Pennie, Davis, Marvin & Edmonds, and Humes, Smith & Tweed, and in addition my attention has been called to an article by Dr. A. Mestern, published in the *Chemische Industrie* of Berlin, in which he also arrives at the conclusion that the title of The Foundation to its patents is valid and that it "will be accordingly in a position to fulfill its aim."

Believe me,

Very truly yours,
Ramsay Hoguet

FIRE CAUSED BY YELLOW PHOSPHORUS

Editor of the Journal of Industrial and Engineering Chemistry:

The communication by H. LeB. Gray in the February number of This Journal on a fire in the organic research laboratory of the Eastman Kodak Company, which fire was caused by yellow phosphorus, reminds me of a somewhat similar fire we had in this laboratory a few years ago. This started in a storeroom hood in which was kept our stock of potassium, sodium, and phosphorus. A danger not mentioned by Mr. Gray came to light in our case. The heat caused a sealed fruit jar containing yellow phosphorus under water to break. The melted phosphorus ran down a drain pipe, of which we were not made aware until the iron trap in which the phosphorus pellets had lodged rusted out later. The plumber, not knowing the character of the phosphorus, was going to throw the fragments of trap with phosphorus content into a waste jar containing combustible matter. The presence of the writer at the psychological moment prevented another fire. The point to be made is that in case of such phosphorus fires as is described it is advisable to follow through the plumbing system and clean out all traps and other lodging places, and dispose of the phosphorus by setting fire to the rubbish, preferably out of doors.

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[1] *Loc. cit.*

[2] Kremers and Schreiner, *Pharm. Rev.*, **14** (1896), 221; Allen, "Commercial Organic Analysis," 4th Ed., **4**, 399

[3] *Bulletin* **3** of the Chemical Foundation, Inc., February 1, 1920.

W. Segerblom

Department of Chemistry, Phillips Exeter Academy
Exeter, N. H., February 7, 1920

THE CHEMICAL INDUSTRY AND TRADE OF SPAIN

The following additional information on "The Chemical Industry and Trade of Spain" was received too late for incorporation in the original article, pp. 226 and 227 of this issue.

Imports of Chemicals and Allied Products

	1913 Lbs.	1916 Lbs.
Oils and Oilseeds, Fats and Waxes:		
Paraffin		
Austria-Hungary	1,481,848	.....
Germany	952,985	.....
United Kingdom	1,536,720	1,575,293
United States	7,234,445	12,922,416

Exports of Chemicals and Allied Products

	1913 Lbs.	1916 Lbs.	1918 Lbs.
Chemicals, Drugs, Medicines:			
Saffron	214.375	193,750	161,980
Argentina	29,079	35,104	...
Cuba	12,566	16,506	...
France	158,018	104,792	...
United Kingdom	6,878	5,743	...
United States	1,303	5,886	...
Oils, Oilseeds, Fats and Waxes:			
Olive Oil	66,578,497	195,885.157	51,697,215
Argentina	17,015,940	22,945,612	.....
Cuba	9,248,432	16,409.510	.....
France	9,761,797	32,666,552	6,149,306
Italy	8,284,817	51,912 313	.....
United States	1,725,160	21,547,593	.....

RAMSAY MEMORIAL FUND

The United States Committee on the Ramsay Memorial Fund has transmitted £3,500 which it has collected; £263 have been sent direct by contributors; and approximately £100 remain in the hands of the Treasurer, W. J. Matheson. Professor Baskerville, the chairman, hopes that the total American contribution, £3,863, may be raised to £4,000, after which the American subscriptions may be closed. The total fund now amounts to £51,274.

This is a very gratifying tribute to the memory of Sir William Ramsay, who did so much for pure science as well as for the cause of the Allies during the recent war.

NATIONAL FOREIGN TRADE COUNCIL REPORT

The Committee on Foreign Chemical Trade of the American Chemical Society calls attention to a recent publication of the National Foreign Trade Council embodying the results achieved by the conference on the "Standardization of Export Quotations and American Export Practice" which was participated in by the nine great foreign trade organizations of the United States. The definitions and recommendations of this conference tend materially to clarify a situation which by its confusion has done much to harm the best interests of American foreign trade. These recommendations urge the formulation by the seller of complete and specific conditions under which his sales are made, and its fifteen page report deals entirely with the standardization of these conditions.

A copy of this valuable report should be in the hands of every one in any way engaged in foreign trade either as importer or exporter, and the Committee would advise all interested to procure a copy, which may be obtained by addressing the National Foreign Trade Council, No. 1 Hanover Sq., New York City.

POSITIONS FOR EX-SERVICE MEN

The War Department, in its endeavor to assist ex-service men in securing positions, has issued the following list of men of various qualifications who are now available. Any member of the Society who is interested in securing such men should communicate with the Service and Information Branch of the War Department.

Accountants	24
Advertisers	3
Agriculturists	5
Auto Mechanics	6
Automobile Salesmen	
Aviators	4
Bacteriologists	3
Bookkeepers	6
Cattlemen	2
Chemists	15
Civil Engineers	25
Clergymen	1
Clerks (General Office Work)	48
Commercial Traffic	5
Construction Engineers	13
Correspondence Clerks	4
Dentists	3
Editors and Reporters	8
Efficiency Engineers	1
Electrical Engineers	11
Executives	7
Exporters and Importers	3
Foremen	14
Forestry Experts	3
Industrial Engineers	2
Insurance Agents	4
Lawyers	23
Linguists	8
Lumbermen	2
Mechanical Engineers	13
Mechanics	5
Mining Engineers	6
Miscellaneous	155
Musicians	3
Oil Miners	2
Physical Instructors	8
Physicians	25
Production Engineers	3
Purchasing Agents	5
Railroad Men	8
Real Estate Agents	1
Roentgenologists	1
Special Investigators	6
Salesmen	26
Sanitary Engineers	2
Statisticians	2
Steam Shovel Men	1
Stenographers	7
Students	34
Teachers	3
Telephone Linemen	2
Undertakers	2
Veterinarians	3

FELLOWSHIP AT WASHINGTON UNIVERSITY

The Monsanto Chemical Company has established in Washington University, St. Louis, Mo., a $500 fellowship in chemistry for the academic year 1920–21. The holder is to be designated by the Chancellor of the University and Professor L. McMaster, and shall be pledged to devote himself exclusively to study and research in chemistry.

DYE SECTION, AMERICAN CHEMICAL SOCIETY

The second meeting of the Dye Section will be held in St. Louis, beginning Wednesday, April 14, 1920. At this meeting the Committee on Permanent Organization will submit "By-Laws" for the consideration of the Section, the approval of which, by the Section and by the Council will be the necessary steps to the permanent organization of the dye chemists of the United States, as the Dye Division of the American Chemical Society.

The secretary asks all scientific workers in the field of dyes to present the results of their researches and experiences at these meetings of the dye chemists. Papers on the manufacture, properties, or application of dyes, both of coal-tar or natural origin, will be of timely interest. Any chemist having any such scientific information ready for presentation is asked to communicate at once with the secretary, giving subject and time for presentation.

As is usual, full details of the final program, time and place of meeting can be obtained by addressing Dr. C. L. Parsons, 1709 G Street, N. W., Washington, D. C., or the undersigned.

43 Fifth Avenue, New York, N. Y.
February 16, 1920

R. Norris Shreve,
Secretary

CALENDAR OF MEETINGS

American Electrochemical Society—Spring Meeting, Boston, Mass., April 8 to 10, 1920.

American Chemical Society—Fifty-ninth Meeting, Hotel Statler, St. Louis, Mo., April 10 to 17, 1920.

American Drug Manufacturers' Association—Annual Meeting, Hotel Biltmore, New York, N. Y., April 12 to 15, 1920.

Technical Association of the Pulp and Paper Industry—Spring Meeting, Hotel Waldorf and Hotel Astor, New York, N. Y., April 12 to 16, 1920.

National Fertilizer Association—27th Annual Convention, White Sulphur Springs, W. Va., week of June 21, 1920.

American Institute of Chemical Engineers—Semi-Annual Meeting, Montreal, June 21 and 22; Ottawa, June 23; Shawinigan, June 24 and 25; La Tuque, June 26, 1920.

WASHINGTON LETTER

By J. B. McDonnell, Union Trust Building, Washington, D. C.

The Senate Finance Committee has favorably reported to the Senate the Longworth dye bill and the measure providing for the protection of chemical and laboratory glassware and scientific instruments.

The Senate Military Affairs Committee has finished its work on the army reorganization measure, and in the bill it reported to the Senate provided for a separate Chemical Warfare Service of the Army. Although there is some opposition to the establishment of the Chemical Warfare Service as a separate department of the Army among members of the House military committee, which still is at work on its draft of the Army reorganization bill, supporters of the Chemical Warfare Service are confident that they will succeed in establishing it as a separate department.

Thus briefly might be summarized events of importance to the chemical world which have taken place in Washington recently. Each step has been won against determined opposition from one quarter or another. Victory for the chemical industry has been the result each time so far, and indications are that victory will continue to perch upon the banners of the industry. Chemistry and the chemical industry have come into their own in Washington and both executive and legislative branches of the Government admit their importance to the nation.

It is planned to call the dye bill up on the floor of the Senate as soon as possible. With Republican and Democratic members of the Finance Committee endorsing the completed measure, little opposition is expected and it will be passed with little delay once it is called up on the floor. If present plans do not miscarry, the end of February will see the bill finished and signed by the President.

As finally drawn up by the committee the bill differs in many respects from the form in which it was passed by the House. The original licensing system was eliminated entirely. After considerable discussion on various substitutes proposed for this section the committee rewrote the entire section. The bill provides that no dyestuffs shall be admitted to import which are obtainable in this country on satisfactory terms as regards quality, price, and delivery.

The life of the law is fixed at three years. The bill defines what is meant by reasonable terms as to price, quality, and delivery. Much is left to the discretion of the United States Tariff Commission, which is charged with administering it. This was done purposely so as to permit of an elasticity in enforcing the provisions and to permit such changes in its rules and regulations governing importation of dyestuffs and coal-tar chemicals as the Commission might find necessary from time to time to meet changed conditions or unexpected contingencies which might arise.

The bill differs from the so-called Choate substitute, in that it does not provide that the Commission shall prepare any lists of what are and what are not importable dyestuffs, leaving it to the discretion of the Commission itself to frame such rules and regulations as it deems best to carry out the provision that no dyes obtainable in this country on reasonable terms as to price, quality, and delivery shall be imported.

It provides also against excessive imports. The committee decided that a reasonable price shall be that which in the judgment of the Tariff Commission is the lowest which will insure the maintenance of the dye industry in this country. Briefly the bill gives large authority to the Commission to decide practically all questions as they arise, setting forth general principles for the guidance of the administering body.

The bill was amended but slightly by the full committee, the work of the sub-committee meeting with general approval. Probably the most important change made was the reduction of the tariff rates in the bill as it passed the House to the same rates which now are in effect; these were enacted in 1916 in the so-called Hill bill. At hearings before both House and Senate committees strong emphasis was laid upon the importance of protecting the industry with a strong "secondary defense." The House accepted the rates as did the Senate dyes sub-committee. The change in the full committee, it is understood, was made as a bid for Democratic support of the measure. Reduction of the duties in the bill to those now in effect enabled the committee to obtain a unanimous favorable report.

An effort to increase the rates probably will be made on the Senate floor. After passage by the Senate the bill will go back to the House for agreement on the Senate amendments. Representative Longworth, author of the original bill, already has been consulted by Senate members and has expressed approval of the bill and little difficulty is expected in the conference committee which will be appointed by the two bodies to iron out the differences.

The President already has put himself squarely on record as in favor of protection of the American dye industry and is expected promptly to sign the measure when it reaches him.

Section 38 of the army reorganization bill reported by the Senate Military Affairs Committee provides for the Chemical Warfare Service.

> The permanent personnel of the Chemical Warfare Service shall hereafter consist of one Chief of Chemical Warfare, with the rank of brigadier-general, and one hundred and twenty-five officers, in grades from second lieutenant to colonel, inclusive, and one thousand two hundred enlisted men, in their appropriate grades, all of whom shall be detailed or assigned from the permanent personnel under the provisions of this Act. The reserve personnel of the Chemical Warfare Service shall consist of all reserve officers and reservists assigned thereto as provided for in this Act.

The Chief of the Service would be selected by the President for a period of four years, unless sooner removed, under the bill. Senator Wadsworth, chairman of the Military Affairs Committee, is confident that the measure will go through the Senate with the Chemical Service a separate department and not as advocated by Chief of Staff March, a subordinate branch of the Ordnance Department.

Beyond question the war with Germany has strongly stamped upon the minds of members of Congress the vital importance to the national safety and welfare of chemistry in practically all its branches and they are not willing to permit a branch of the war-making machine of the country, which is certainly destined to play so important a part in whatever wars come in the future, to be made simply a branch of another department of the War Department.

Following conclusion of its consideration of the dyestuffs bill the Senate Finance Committee immediately took up the sub-committee report on the bill providing for the protection of the chemical glassware, porcelain ware, scientific and surgical instruments. This bill introduced in the House by Representative Bacharach was passed by that body several months ago and has been before the Senate committee since that time. Action on this and other tariff bills which had been passed by the House was delayed, however, pending the disposition of the dye bill which was properly deemed the most important of the tariff measures.

Favorable report on the Bacharach glassware bill has now been ordered by the Finance Committee and it will be taken up on the Senate floor in the near future. Passage of this measure also is assured, there having developed no real opposition to it. The committee reported the bill without amendment.

The Federal Trade Commission has been active during the last month and has cited several chemical and dyestuff concerns on charges of commercial bribery. Practically all of these firms are located in New York City. The list of the firms cited does not include the names of the largest companies, but is confined for the most part to the dealers in dyestuffs. Hearings on several of the cases have been held before the Commission but as yet there have been no orders issued in the cases. Hearings before the Commission are not made public, only the result being given. Orders to cease and desist practices now indulged in by these firms are expected to be issued within a comparatively short time.

Representatives of the firm of Kuttroff and Pickhardt, dye importers, who have been mentioned many times in connection with the efforts of the German chemical cartel to reëstablish its hold on the American market, appeared before the War Trade Board recently to answer charges of interfering with the efforts of this country to obtain needed German vat colors. The hearings occupied two full days. What action will be taken by the War Trade Board is not known. Officials are emphatic in their refusal to discuss the case, declaring they can see no reason why they should depart from the custom held to throughout the war and make any public announcement regarding this case. It will be recalled that Francis P. Garvan charged before the Senate dyes committee that the activities of the firm were largely responsible for the delay in getting German dyes into this country in spite of government efforts. Mr. Garvan's charge, together with cables which he produced before the committee, have already been published. Accompanied by their attorney, members of the firm attempted to justify the actions which brought about the charge and consequent hearings on them. The hearings were held strictly confidential. The War Trade Board can refuse to permit the firm to import any enemy dyestuffs so long as its authority continues.

Cabled advices received recently state that German dyes obtained under the reparations commission now are in large part in Rotterdam and should be in this country within a short time.

February 14, 1920

INDUSTRIAL NOTES

The Foreign Commerce Corporation of America has been organized by interests identified with J. P. Morgan & Co. The corporation is designed to enter trade in Europe on a large scale and under plans that may lead to the extension of long credit to manufacturers and merchants in the war zone. E. R. Stettinius will be chairman of the executive committee.

A recent fire in the vegetable oil refinery of Swift & Co., Memphis, Tenn., destroyed the refinery, machinery and contents and 400,000 pounds of vegetable oil, with a loss of approximately $150,000.

The United States Rubber Company has purchased the entire plant and business of the Dolgeville Felt Shoe Co., Dolgeville, N. Y., manufacturers of felt shoes and slippers.

The annual dinner of the officers of the Chemical Warfare Service was held at the New Ebbitt Hotel, Washington, on the evening of January 2, 1920. Major-General William Sibert, director of Chemical Warfare Service, presided.

Classification of the drug industry by branches, for purposes of the 1919 census of manufactures, has just been completed by the Census Bureau. More than 350 classifications have been provided for convenience in separating industries. As a general rule, the classification of an industry will be determined in accordance with the product of chief value.

The Monsanto Chemical Co., St. Louis, Mo., has issued an order stating that none but Americans will be employed in its plant, and requiring any alien employee to be naturalized or accept thirty days' notice of discharge. The notice reads: "It is the desire of this company to have associated with it only American-born or naturalized American citizens. The Monsanto is an American institution and is firm in its desire to be American in all its work and operations. The employees' department will assist any employee in perfecting his or her American citizenship."

The California Prune and Apricot Growers' Association is to erect at Hemet, Cal., a factory for using apricot pits in the chemical and dye industries. Hemet is the largest apricot growing center of Southern California.

The American Institute of Mining and Metallurgical Engineers has announced that the symposium on the subject of Pyrometry held in coöperation with the National Research Council and the National Bureau of Standards at the Chicago Meeting of the Institute in September 1919, will be published as a special volume, comprising about 750 pages. Subscription price, previous to publication, is $5 per volume.

The National Organization for Public Health Nursing has announced that an Industrial Nursing Section is to be formed at the meeting in Atlanta, April 12 to 17, 1920, with the object of making known to nurses throughout the country the opportunities for education as industrial nurses. Uniform standards of service and better preparation are needed in this field.

The Burrell Technical Supply Company has been organized with offices in Pittsburgh, Pa., to conduct a general laboratory and technical supply business. The officers of the company are Col. G. A. Burrell, President; J. T. Ryan, Vice President; G. H. Deike, Treasurer; and G. C. Nelms, Secretary. Catalogs will be issued shortly, one of the first being devoted to gas analysis apparatus.

Bids will be opened March 10 for supplying the government departments in Washington with drugs, medicines, and chemicals. The quantities to be purchased are indefinite, but are estimated on the basis of purchases during the fiscal year 1919.

E. I. du Pont de Nemours & Company has purchased a $140,000 warehouse in the central manufacturing district of Chicago for use as a general warehouse.

The United States is the world's largest consumer of crude cocoa, the consumption for 1918 being 386,000,000 lbs., or 50 per cent of the total world production. For the fiscal year ending in June 1919, 313,037,419 lbs. of crude cocoa were imported, 32,709,845 lbs. of which were reëxported, making the apparent consumption of crude cocoa for 1919 approximately 280,000,000 lbs. In spite of the decreased amount of crude cocoa available, the value of exports of prepared cocoa rose from $6,000,000 in 1918 to $11,000,000 in 1919.

The General Chemical Company has just issued its annual report to the stockholders. The report shows a general decline in profits due to rising cost of production without corresponding rise in prices. The Company has recently declared a quarterly dividend of 2 per cent on common stock, payable March 1, 1920.

A large Oriental copra corporation has begun construction of a large plant on Richmond Harbor, Cal., for the handling of copra. Two large copra plants are already established at Richmond, one of them belonging to Procter & Gamble.

A scarcity of olive oil in Sydney, Australia, has been reported, the market relying largely on importations from Italy and Spain in the failure of the South Australian product.

According to a report by the president of the Board of Agriculture to the New Zealand House of Representatives, the phosphate reserves of the Island of Nauru in the Pacific are sufficient to meet the demands of the world for 200 years. 80,000 to 100,000 tons or more are available, and the quality is said to be of the highest grade. The average yearly production is now in the neighborhood of 150,000 tons.

The Pacific Chemical Co., of Los Angeles, Cal., has recently been organized with a capital of $50,000.

The Federal Trade Commission has entered charges of unfair methods of competition against the following companies·

United Chemical and Color Company, New York City
Andreykovicz and Dunk, Inc., Philadelphia
Arkansas Distributing Company, New York City
F. Bredt and Company, New York City
New York Color and Chemical Company, New York City
H. Behlen & Bros., Inc., New York City
Franklin Import and Export Company, Inc., New York City
Heller & Merz Co., New York City
Shibakawa and Company, Inc., New York City
Taiyo Trading Co., Inc., New York City

The companies have forty days in which to file answers, after which time the cases will be set down for trial. The Plomo Specialty Manufacturing Co. and the Riverside Refining Co., of Cleveland, Ohio, have been ordered to cease from unfair methods of competition in the manufacture and sale of turpentine and oils. C. Bischoff & Co., of New York City, manufacturers of dyestuffs and chemicals, have been ordered to refrain from unfair competition in interstate commerce.

The National Research Council has announced an exhibit of the wireless telephone at 1201—16th St., N. W., Washington, D. C., beginning February 6, 1920. The exhibit includes special apparatus reproducing fundamental electrical discoveries in the development of the wireless telephone, moving line-drawing illustrating wireless telephone action, portraits of scientists who have contributed to its development, and wireless telephones which visitors may use. The exhibit was installed by the American Telephone & Telegraph Co. and the Western Electric Co. with the coöperation of the Signal Corps and the Air Service of the U. S. Army.

Damage estimated at $50,000 was caused by a fire which followed an explosion of tanks of acid at the Naugatuck Chemical Company, Naugatuck, Conn., recently.

101,221,784 barrels of crude oil were produced in California in 1919 compared with 101,637,870 barrels in 1918. Oklahoma is the only other state with a yearly production in excess of 100,000,000 barrels.

The United States Civil Service Commission has announced that the government service needs a large number of chemists, physicists, metallurgists, electrical laboratorians, etc. Further information and application blanks may be obtained from the U. S. Civil Service Commission, Washington, D. C.

The U. S. Civil Service Commission has announced a competitive examination, open to both men and women between 18 and 35 years of age, for laboratory assistant, at a salary of $900 to $1200 a year. Persons unusually qualified may be appointed at a higher salary. Applications must be filed with Civil Service Commission, Washington, D. C., on or before March 9, 1920.

At the suggestion of Herbert C. Hoover, president-elect of the American Institute of Mining Engineers, coal operators from all over the country met at New York, February 17 to 18, to discuss the stabilization of the coal industry. The meeting was addressed by Dr. Van H. Manning, Director of the Bureau of Mines; Dr. George Otis Smith, Director of the Geological Survey; Professor H. H. Stoek, of the University of Illinois; S. L. Yerkes, Vice President of Grider Coal Fields Co., of Birmingham, Ala.; and A. K. Knickerbocker, of the Missouri School of Mines.

The Reliable Chemical Products Corporation has been chartered in Delaware with $100,000 capital for the manufacture of chemicals.

The Grasselli Chemical Company and the Sterling Products Company of Rensselaer, N. Y., are planning extensive additions to their plant. A new railroad spur track has been constructed, and new building are to be built on land adjoining the present plant.

Hemingway & Co., a prominent New York dyestuff and chemical house, has recently been merged with the Sherwin-Williams Co. The Hemingway & Co. plant at Bound Brook, N. J., will be operated as a separate company. The merger was preceded by the absorption by Hemingway & Co., of Frank Hemingway, Inc., a selling company, and Frank Hemingway, manager of that company, will act as manager of the development department of the Sherwin-Williams Co.

The British Dyestuffs Corporation Board of London has announced a dividend of 8 per cent on £4,077,000 preferred capital, after paying 7 per cent on £4,106,000 preference capital. No dividend has been announced on the £980,000 deferred.

The Bureau of Standards has announced the installation at Petrolia, Texas, of an apparatus for continuously recording the percentage of helium in a gas mixture. Analyses of the natural gas used at the plant in the extraction of helium on a large scale are frequently required in order to control the operation and the new recorder has proved its superiority over the lengthy processes formerly used.

A committee of expert users of dyes, consisting of representatives of English textile, woolen, cotton, paint, and varnish industries is going to Germany in behalf of the London Board of Trade to purchase £2,000,000 worth of five dyestuffs. Purchases will be in addition to the 1,500 tons assigned to British consumers under the Reparation Clause of the Treaty.

PERSONAL NOTES

Dr. Francis C. Phillips, aged 69 years, expert on chemistry, died at his home in Pittsburgh, Pa., on February 16, 1920, of influenza and pneumonia. In 1875 he left Delaware College, Wilmington, Del., where he was in charge of the Chemistry Department, to go to the University of Pittsburgh, where he was professor of chemistry for forty years.

David S. Pratt, 34 years old, former professor of chemistry at the University of Pittsburgh, died of pneumonia on January 28, 1920, at his home in St. Louis. Dr. Pratt was a graduate of Cornell University and did work in European schools.

Dr. David Moore Balch, scientist who perfected the extraction of potash from kelp, died in San Diego, Cal., November 17, 1919.

Dr. S. Mackay, professor of chemistry at Dalhousie University since 1896, died from pneumonia in Halifax, N. S., on January 6. Dr. Mackay was born in Nova Scotia in 1864 and was educated at Dalhousie and Johns Hopkins Universities.

At the Mid-Year Commencement Exercises of the University of Pittsburgh, on February 19, honorary degrees were conferred upon **Dr. William Henry Nichols**, past president of the AMERICAN CHEMICAL SOCIETY and **Dr. William Albert Noyes**, present president, upon the recommendation of the Mellon Institute of Industrial Research.

In presenting Dr. Nichols to Chancellor Samuel Black McCormick, Director Raymond F. Bacon said:

> I have the honor to present for the degree of Doctor of Science the Field Marshall of American Chemical Industry, Dr. William Henry Nichols, Chairman of the Board of Directors of the General Chemical Company and respected counselor in the administrative conduct of an assemblage of other great corporations This distinction is most appropriately bestowed upon Dr. Nichols in recognition of his activities in opening up fields for research during the course of developing our key-industries. But while gaining a world-wide reputation as a chemical industrialist, Dr. Nichols has also found time constantly to advocate the orderly synthesis of the sciences in inquiries of technologic concernment and to advance ardently the best interest of the chemical profession. He has rendered inestimably valuable service as president of the Society which he participated in organizing, namely, the AMERICAN CHEMICAL SOCIETY; and he has also served with eminence as president of the Society of Chemical Industry and as president of the Eighth International Congress of Applied Chemistry.

Director Bacon introduced Dr. Noyes as follows:

> It affords me great pleasure to present for the degree of Doctor of Chemistry the distinguished successor of Dr. Nichols as president of the AMERICAN CHEMICAL SOCIETY, Dr. William Albert Noyes. Dr. Noyes stands in the forefront of the chemical profession as one of the most erudite investigators, and, as the active Director of the Chemical Laboratory of the University of Illinois, he has rendered noteworthy service in the teaching of chemistry and in the training of research men. In addition, from 1902 to 1917 he was the eminently successful editor of *The Journal of the American Chemical Society*, in which positional capacity he devoted his best energies to the advancement of chemical knowledge and thought. There are, indeed, few scientists who have accomplished so much through their own efforts.

Dr. A. V. H. Mory, formerly chief chemist of Sears, Roebuck & Co., Chicago, Ill., has been appointed administrative head of the chemical division of Procter & Gamble Co., Ivorydale, Ohio. Associated with Dr. Mory in this work is Mr. H. J. Morrison who has been appointed special and consulting chemist for the company.

At a recent meeting of the executive committee of the Corporation of the Massachusetts Institute of Technology, it was decided that no acting president is to be appointed to fill the vacancy caused by the death of Dr. Richard C. Maclaurin. The executive committee has appointed an administrative committee consisting of **Dr. Henry P. Talbot, Prof. Edward F. Miller,** and **Dr. William H. Walker**, which will be charged with those duties ordinarily performed by the president in relation to the international and educational affairs of the Institute. A subcommittee has also been elected consisting of **Messrs. Morss, Hart** and **Webster**. It is the belief of the executive committee that its sub-committee working in close association with the administrative committee will make it possible to carry on the work of Technology without any interruption and with complete harmony and effectiveness.

Mr. Harvey J. Skinner, for many years vice president of Arthur D. Little, Inc., Cambridge, Mass., has severed his connection with that organization and has opened an office as a consulting chemical engineer in Boston, Mass.

Mr. Richard H. Catlett, formerly assistant engineer of the International Coal Products Corporation, Irvington, N. J., recently became partner in Charles E. Richardson & Co., Engineers, New York City.

Mr. G. A. Williams, formerly assistant chief chemist at the Atlas Crucible Steel Co., Dunkirk, N. Y., is now in charge of the heat treating department of the Rich Steel Products Co., Battle Creek, Michigan.

Mr. John Gore, formerly with the Chemical Warfare Service and later chief chemist for the Pawtucket Gas Co., Pawtucket, R. I., is now chief chemist and chemical engineer for the Russ Gelatin Co., Westfield, Mass.

Mr. Edwin J. Mullen, recently discharged from the U. S. Army, has rejoined the General Chemical Co. as superintendent of their Camden Works, Camden, N. J.

Mr. C. E. Mangels is at present located in Washington, D. C., where he has accepted the position of investigator in commercial dehydration, Bureau of Chemistry.

Mr. H. F. Fish, formerly in the research department of the Great Western Sugar Co., Denver, Colorado, has been appointed by the Board of Trustees of the University of Illinois as special research assistant in the joint investigation of the fatigue of metals and is located at Champaign, Illinois.

Mr. Kent H. Smith, since returning from France as Lieutenant in the Air Service, attached to the Courier Service, has been in the employ of the Dow Chemical Co., Midland, Michigan.

Mr. W. H. Dickerson, actively engaged in the recovery of industrial waste for a number of years, especially waste sulfite liquor in the pulp and paper industry, has joined the Industrial Waste Products Corp., of New York City.

Mr. J. Howard Roop, former chief chemist of feedingstuffs in the state chemists' department of Purdue University, has accepted a place as chief chemist of the Nobelsville Milling Co., Nobelsville, Indiana. He is installing a laboratory in the company's new office building and will do research work in flour, milling and baking.

Mr. Albert E. White, formerly head of the metallurgical branch, technical staff of the Ordnance Department, has returned to his former position as professor of chemical engineering at the University of Michigan, Ann Arbor, Michigan. Mr. White is also consulting engineer to the Detroit Edison Company and the Packard Motor Car Company.

Mr. H. DeWitt Valentine has resigned from his position as instructor in chemical engineering at the University of Wisconsin, Madison, Wis., and is now retained as chemical engineer and bacteriologist by the Ozone Company of America, Milwaukee, Wis.

Dr. A. S. Eastman, recently connected with the Hercules Powder Co., where he was engaged during the war upon the manufacture of TNT, has joined the forces of the Calco Chemical Co., Bound Brook, N. J., where he is in charge of the chemical control work.

Mr. George Weintraub, formerly chief chemist of Rare Metals Co., Perth Amboy, N. J., is now metallurgical chemist of the Standard Chemical Co., Canonsburg, Pa.

Mr. Edwin Smith, Jr., formerly in the Chemical Warfare Service, has resumed work with Mr. Thomas A. Edison at his laboratory in West Orange, N. J.

Mr. W. E. Burkhard is chemical engineer at the Perth Amboy Chemical Works, Perth Amboy, N. J., having formerly been chief chemist at Baker & Adamson Co., Easton, Pa.

Mr. R. F. Brenner, now connected with the Bartlett-Collins Glass Co., of Sapulpa, Okla., as chief chemist, was formerly employed as assistant chemist by the H. C. Fry Glass Co., of Rochester, Pa.

Mr. Sherman Leavitt, who for the past eight years was professor of chemistry and agriculture in Illinois College, Jacksonville, Ill., and later chemist to the Connecticut State Board of Health, has become food chemist for the War Department, stationed in the Bureau of Chemistry laboratory at St. Louis, Mo.

Mr. Stuart B. Marshall, consulting engineer, chemist and metallurgist, was formerly general superintendent of the Aluminum Company of America's business at North Carolina and now has his headquarters at Cleveland Park, Washington, D. C.

Mr. A. N. Finn, previously associate chemist with the U. S. Bureau of Standards, resigned last October from that position to accept employment in the research department of the Hydraulic Pressed Steel Co., of Cleveland, Ohio.

Mr. H. C. Bradley has left the Chemical Warfare Service at Washington, D. C., and has returned to his former position, that of professor of physiological chemistry, Medical School, University of Wisconsin, Madison, Wisconsin.

Mr. Lansing S. Wells, formerly assistant and fellow in the department of chemistry, University of Illinois, Urbana, Ill., is at present employed as research chemist for the Barrett Co., chemical department, Frankford, Philadelphia, Pa.

Mr. E. B. Clark has severed his connection as chemist with the Ward Baking Company, New York City, and has joined the staff of the Omaha Flour Mills Co., Omaha, Nebraska.

Mr. Francis J. Curtis, who for the last four years has been doing research work at the South Wilmington plant of the Merrimac Chemical Co., of Boston, Mass., recently joined the staff of the Westport, Conn., mill of the Dorr Company to do industrial research work.

Mr. E. L. Hutchins, formerly with the Anderson Phosphate and Oil Co., Anderson, S. C., has returned to the employ of Law and Co., Wilmington, N. C.

Mr. Floyd E. Rowland, formerly in the research division, Chemical Warfare Service, and more recently in the chemistry department of the Oregon Agricultural College, is now associated with the University of Kansas, Lawrence, Kansas, as assistant professor of chemistry.

Mr. Clinton V. Conley, formerly assistant chemist at the Puget Sound Navy Yard, was recently transferred to the Chicago Meat Inspection Laboratory of the Bureau of Animal Industry, where he is employed as assistant chemist in charge of the analysis of fats and oils.

Mr. Martin L. Griffin, who has been associated with the pulp and paper industry for many years and also with the Oxford Paper Company of Rumford, Maine, since 1910, has resigned his position as manager of the chemical and electrochemical departments of that firm and has taken a position as expert chemical process engineer with the Mount Hope Finishing Company of North Dighton, Mass.

Mr. Thomas E. Comerford, formerly chief inspector for the U. S. Army at the Nobel Ontario Plant of the Canadian Explosives, Ltd., is at present chemist with the Aetna Explosives Co., where he is stationed at their Fayville, Illinois, plant.

Mr. H. T. Buchanan who prior to the war was connected with Warner Moore & Co., of Richmond, Va., is now with the Texas Star Flour Mills, Galveston, Texas.

Mr. Wallace H. Dickhart, formerly with the Pease Laboratory as food and water chemist, is now connected with the Bureau of Chemistry of the New York Produce Exchange, New York City.

Mr. W. F. Zimmerli has severed his relations as chief chemist of the International Pfaudler, Ltd., and has accepted a similar position with the Howe Rubber Co. New Brunswick New Jersey.

Mr. E. N. Ehrhart has resigned as chief chemist and efficiency engineer with the Sterling Sugar & Railway Co., Franklin, La., and has become chemical technologist in charge of the construction of equipment and operation of a molasses treatment and raw sugar washing plant for the Dunbar Molasses & Syrup Co., New Orleans, La.

Mr. Seth S. Walker resigned as soil chemist to the Louisiana Agricultural Experiment Station, Baton Rouge, La., to become chemist to the Florida Citrus Exchange and Exchange Supply Co., with laboratory and headquarters at Tampa, Florida.

Dr. H. S. Adams, formerly production manager of E. R. Squibb & Sons, New York City, is director of research with the Naugatuck Chemical Co., Naugatuck, Conn.

Mr. John H. Gardner left his position as analytical chemist for the Cleveland Provision Co., Cleveland, O., to take a similar position with the Ault and Wiborg Co., Cincinnati. Ohio.

Dr. Allen E. Stearn, of the chemistry department of the University of Illinois, has taken charge of the division of physical chemistry at the University of West Virginia.

Mr. H. J. Morrison, of the Procter & Gamble Co., Ivorydale, O., has been appointed Special and Consulting Chemist for this Company. This appointment comes as a just recognition of Mr. Morrison's well-known, broad experience covering many years in the technology of soap and allied products.

Dr. E. H. Leslie has resigned his position as assistant to the president and general manager of the U. S. Industrial Alcohol Co., New York, and has accepted a position as associate professor of chemical engineering in the department of chemical engineering at the University of Michigan, Ann Arbor, Michigan. In addition to Dr. Leslie's university duties he will engage in consulting work.

Dr. H. A. Morton severed his connections with the Mellon Institute of Industrial Research as industrial fellow, and has accepted the position of director of the research laboratory of Miller Rubber Co., Akron, Ohio.

Mr. Charles S. Ash has retired from the firm of Gould and Ash, San Francisco, Cal., and Mr. Ralph A. Gould will continue the business under his own name.

Mr. J. R. Hess, who was formerly chief chemist of the Omaha Flour Mills Co., Omaha, Neb., is at present employed as chief chemist of the Reno Flour Mills Co., Hutchinson, Kansas.

Mr. Frank C. Gutsche resigned his position as chemist for the Wolverine Oil Co., Tulsa, Okla., to acccept a position in the chemical research department of the Western Electric Co., Chicago, Illinois.

Mr. Frederic W. Murphy recently severed his relations with the American Sugar Refining Co., New York City, and has taken the position of general manager of business and manufacture of the Virginia Fruit Juice Co., Norfolk, Virginia.

Mr. K. J. Thompson has changed his position from superintendent of the Columbia Tire & Rubber Co., Columbiana, O., to factory manager of the Mansfield Tire & Rubber Co., Mansfield, Ohio.

Dr. Alcan Hirsch has incorporated his laboratory under the name of Hirsch Laboratories, Inc., with office in New York City and laboratories in Brooklyn. The officers of the firm are as follows: **Alcan Hirsch**, president; **Marx Hirsch**, vice president; and **Harry W. Wolff**, general manager.

Dr. Edward Ardern, F.I.C., formerly chief chemist, has been appointed consulting chemist to the Rivers Committee of the Manchester Corporation, and has joined Mr. S. E. Melling, F.I.C., consulting chemist to the Salford Corporation, public analyst for the County of Chester, etc., in practice as analytical and consulting chemists, at Manchester, England.

Mr. Arthur Phillips has resigned his position as metallurgist of the Bridgeport Brass Co., Bridgeport, Conn., to become assistant professor of metallurgy, in the Sheffield Scientific School, Yale University, New Haven, Conn.

Mr. R. H. Bullard, formerly instructor in chemistry at Hobart College, Geneva, N. Y., has accepted a position in the research department of the Roessler & Hasslacher Chemical Co., Perth Amboy, N. J.

Dr. E. R. Pickrell has been connected with Du Pont-Young Corp., Boston, Mass., since resigning from the position of chief chemist of the U. S. Customs Service, Port of New York, in March 1919.

Dr. Henry R. Curme has left the Mellon Institute, Pittsburgh, Pa., and is now with the American Borvisk Co., Cleveland, O., where he is in charge of experimental chemistry.

Dr. C. G. Storm, formerly Lieut. Colonel, Ordnance Department, U. S. A., has resigned as assistant director of research with the Trojan Powder Co., Allentown, Pa., to accept the position of professor of chemical engineering in the Ordnance School of Application, Aberdeen Proving Ground, Maryland, and will also be engaged in research work on explosives and other Ordnance materials.

Mr. James Bradley, formerly connected with the Atlas Powder Co., and later going to the U. S. of America Explosives Plant "C," Nitro, W. Va., as supervisor of sulfuric acid plant, is now connected with the miscellaneous manufacturing department of E. I. du Pont de Nemours & Co., Lodi Works, Lodi, N. J., as plant supervisor, making dyes and intermediates.

Mr. C. S. Moore, formerly connected with the McGraw Tire & Rubber Co., has organized the Corona Cord Tire Co., East Butler, Pa., with three former associates.

Mr. M. C. Burt has severed his connections with the Atlas Powder Co., Landing, N. J., with which firm he was associated as director of their research laboratories, and has accepted a position with the Aetna Explosives Co., in the operating department, at New York City.

Mr. Philip A. Macy resigned as assistant chemist at the Florida Experiment Station, Gainesville, Fla., to take a position with the Florida Agricultural Supply Co., Jacksonville, Fla., as superintendent of their new factory, manufacturing insecticides.

Mr. P. E. Landolt, who has been connected with the Research Corporation, New York City, since its organization and who is thoroughly familiar with the many industrial applications of the Cottrell electrical precipitation processes, has been appointed manager of the commercial department of that concern.

Miss Mildred E. Hinds, formerly chief chemist in the food and drugs department of Tennessee, has accepted the position of chemist and assistant manager with the B. M. Johnson Manufacturing Co., Jackson, Tennessee.

Mr. Norman H. Borden resigned his position as junior chemist with the Insecticide and Fungicide Board. Department of Agriculture, to accept a position in the laboratory of the Sherwin-Williams Co., at their Chicago plant, where his work is chiefly on insecticides.

Mr. J. C. Heckman left his position as consulting engineer of Larkin Company, Buffalo, N. Y. to become production manager for the United Drug Co., Boston, Mass.

Mr. C. B. Worth has resigned as assistant chief metallurgist of the Hudson Motor Co., to accept the position of metallurgist with the International Fabricating Corp., Wilkes Barre, Pennsylvania.

Mr. H. M. Gray, formerly with the Superior Chemical Co., has accepted the position of president and general manager of the Como Chemical Co., Kokomo, Indiana.

Mr. R. S. McBride, engineer-chemist of the National Bureau of Standards, and who for the past several years has prepared the Government Publication section of THIS JOURNAL, resigned January 15, to become the engineering representative in Washington, D. C., of McGraw-Hill Co., of New York City.

Mr. Leon Littell, formerly with the Navy Department in the office of the Purchasing Department at the Brooklyn Navy Yard in a civilian capacity, resigned from that position to accept one as control chemist with the South Porto Rico Sugar Co., at its Guanica Factory, Ensenada, P. R. Mr. Littell's connection with this company ends at the close of the crop season, about June 15, at which time he will return to New York.

GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

CONGRESSIONAL COMMITTEE REPORTS

Tungsten Ores. Hearings before Finance Committee of Senate on House Report 4437 to provide revenue for Government and to promote production of tungsten ores and manufacture thereof in United States. November 10 and 11, 1919. 55 pp.

PUBLIC HEALTH SERVICE

Ultraviolet Rays in Water Purification. Public Health Reports, 34, 2831–2834 (December 12, 1919).

The Public Health Service has received a number of requests regarding the sterilization of water by means of ultraviolet rays. For the information of persons interested in this subject, abstracts of certain articles on this method of water purification are given.

Precautionary Measures to Prevent Lead Poisoning. Public Health Reports, 34, 2905–2907 (December 19, 1919).

The Office of Industrial Hygiene and Medicine of the United States Public Health Service has recently concluded a survey of the pottery industry, located chiefly in Trenton, N. J., and East Liverpool, Ohio. The survey was made with particular view to determining the extent of lead poisoning in this industry, and to give oral and written advice and precautionary instructions.

NATIONAL ADVISORY COMMITTEE FOR AËRONAUTICS

The following are separates from the fourth annual report of this board:

Altitude Laboratory for Testing of Aircraft Engines. H. C. DICKINSON AND H. G. BOUTELL. Report 44. 20 pp. Paper, 10 cents.

Structure of Airplane Fabrics. E. D. WALEN. Report 36. 40 pp. Paper, 10 cents.

Testing of Balloon Gas. J. D. EDWARDS. Report 41. 6 pp. Paper, 5 cents.

New Process for Production of Aircraft-Engine Fuels. A. J. PARIS, JR., AND W. F. PARIS. Report 42. 16 pp. Paper, 5 cents.

Ferrosilicon Process for Generation of Hydrogen. Report 40. 44 pp. Paper, 15 cents.

(1) **Generation of Hydrogen from Ferrosilicon and Sodium Hydroxide.** E. R. Weaver, W. M. Berry and V. L. Bohnson.

(2) **Effect of Presence of Sodium Carbonate on Generation of Hydrogen from Ferrosilicon and Sodium Hydroxide.** E. R. Weaver and B. D. Gordon.

(3) **Use of Lime in Generation of Hydrogen by Use of Ferrosilicons.** B. D. Gordon.

Effect of Compression Ratio, Pressure, Temperature, and Humidity on Power. Report 45. 32 pp. Paper, 10 cents.

(1) **Variation of Horsepower with Altitude and Compression Ratio.** H. C. Dickinson, W. S. James and G. V. Anderson.

(2) **Value of Supercharging.** H. C. Dickinson and G. V. Anderson.

(3) **Variation of Horsepower with Temperature.** H. C. Dickinson, W. S. James and G. V. Anderson.

(4) **Influence of Water Injection on Engine Performance.** V. W. Brinkerhoff.

The following are from the fifth annual report:

Properties and Preparation of Ceramic Insulators for Spark Plugs. Report 53. 35 pp. Paper, 10 cents.

(1) **Methods of Measuring Resistance of Insulators at High Temperatures.** F. B. Silsbee and R. K. Honaman.

(2) **Electrical Resistance of Various Insulating Materials at High Temperatures.** R. K. Honaman and E. L. Fonseca.

(3) **Preparation and Composition of Ceramic Bodies for Spark-Plug Insulators.** A. V. Bleininger.

(4) **Cements for Spark-Plug Electrodes.** H. F. Staley.

Temperatures in Spark Plugs Having Steel and Brass Shells. C. G. Cragoe. Report 52. 8 pp. Paper, 5 cents.

Effect of Temperature and Pressure on Sparking Voltage. L. B. Loeb and F. B. Silsbee. Report 54. 11 pp. Paper, 5 cents.

Subsidiary Gas as Means for Improving Ignition. W. S. Gorton. Report 57. 16 pp. Paper, 10 cents.

GEOLOGICAL SURVEY

Mineral Resources of the United States, 1916. Part I, Metals. 871 pp. The separate chapters of this volume have been reviewed previously.

Our Mineral Supplies. Bibliography compiled under the direction of G. M. Wood. 58 pp.

Water-Power Investigations in Southeastern Alaska. G. H. Canfield. Bulletin 712-B. Separate from Mineral Resources of Alaska, 1918-B. 90 pp.

Geology and Water Resources of the Gila and San Carlos Valleys in the San Carlos Indian Reservation, Arizona. A. T. Schwennesen. Water-Supply Paper 450-A. 27 pp. Contributions to the Hydrology of the United States, 1919. Issued November 10, 1919.

Coal in 1917. Part B, Distribution and Consumption. C. E. Lesher. Separate from Mineral Resources of the United States, 1917, Part II. 57 pp. Issued November 18, 1919.

Manganese and Manganiferous Ores in 1917. D. F. Hewett. Separate from Mineral Resources of the United States, 1917, Part I. 32 pp. Issued October 31, 1919.

Peat in 1918. C. C. Osbon. Separate from Mineral Resources of the United States, 1918, Part II. 25 pp. Issued November 24, 1919.

The quantity of crude air-dried peat produced in the United States in 1918 was 151,521 short tons, nearly 56 per cent more than the record output of 97,363 tons in 1917. Nearly all producers of crude peat in this country use their entire output in the manufacture of peat products, and it was therefore impossible to determine accurately the value of the raw material. However, the average price received for all peat products in 1918 was $9.76 a ton, and the gross market value was $1,047,243, a gain of $2.47 in average price per ton and of $337,343, or approximately 48 per cent, in gross market value, compared with 1917.

Nickel Deposits in the Lower Copper River Valley, Alaska. R. M. Overbeck. Bulletin 712-C. Separate from Mineral Resources of Alaska, 1918-C. Pp. 91–98.

The purpose of the present investigations of the nickel deposits of Alaska is to accumulate data about the extent to which the United States can be independent of other countries for its supply of nickel. Such data are valuable, even if the deposits are never worked, because they may prescribe limits to the monopoly held by other countries. Unless a strong demand for nickel on the Pacific coast should arise through the establishment of industries in which nickel is used, the present known nickel deposits of Alaska probably could not compete, for their nickel content alone, with the deposits of Sudbury, Canada.

Arsenic. J. M. Hill. Separate from Mineral Resources of the United States, 1918, Part I. Pp. 193–194. Issued November 19, 1919.

The white arsenic produced in the United States in 1918 amounted to 6,323 short tons, valued at $1,213,000. This was a slight increase over the output in 1917, which was 6151 short tons, valued at $1,118,313. Besides producing white arsenic one company reported that it produced metallic arsenic.

By far the greater part of the domestic white arsenic consumed in the United States in 1918 was used in preparing insecticides and weed killers, the total quantity so used in 1918 being about 2,000,000 pounds. Nearly 1,000,000 pounds were used in the glass industry, and a small quantity in the preparation of drugs.

The stocks of white arsenic in the hands of producers at the end of 1918 were approximately 449 short tons, or about 7 per cent of the production.

The price of white arsenic was fixed by the Food Administration at 9 cents a pound in carload lots early in 1918, though the price had been as high as 15 cents a pound. Announcement was made on December 12, 1918, of the cessation of price fixing by the Government, and at the same time permission was granted to export arsenic and arsenical insecticides.

Bismuth. J. M. Hill. Separate from Mineral Resources of the United States, 1918, Part I. P. 195. Issued November 19, 1919.

In 1917 bismuth was recovered by only one company in the United States, the American Smelting & Refining Co., which obtains this product from the refining of lead bullion. Statistics of production cannot be published.

Bismuth imported for consumption in the United States in 1918 was 135,700 pounds, valued at $277,273. No exports of bismuth are recorded.

The prices quoted were practically stationary at $3.50 a pound in 500-pound lots throughout the year 1918, though there was a drop to $3.35 a pound in February and March.

Selenium. J. M. Hill. Separate from Mineral Resources of the United States, 1918, Part I. P. 197. Issued November 19, 1919.

The production of selenium in 1918 was 103,694 pounds, valued at approximately $206,540. As compared with 39,630 pounds, valued at $70,000, produced in 1917, this was an increase of 162 per cent in quantity and 195 per cent in value. Selenium was recovered in 1918 as a by-product in the electrolytic copper refineries operated by the Raritan Copper Works, United States Metals Refining Co., Nichols Copper Co., and American Smelting & Refining Co.

Producers reported prices varying from $1.60 to $2.50 a pound. Quoted prices showed as high as $3.25 a pound during the first eight months of the year but dropped to $2.75 a pound during the last quarter.

Tellurium. J. M. Hill. Separate from Mineral Resources of the United States, 1918, Part I. P. 199. Issued November 19, 1919.

There was a small demand for tellurium in 1918, but as only one producer, the Raritan Copper Works, reported production or sale of this metal, it is not possible to give figures showing production. Stocks of tellurium are apparently large as compared with the annual consumption.

Platinum and Allied Metals in 1918. J. M. HILL. Separate from Mineral Resources of the United States, 1918, Part I. Pp. 201–209. Issued December 8, 1919.

Crude placer platinum was produced from mines in Alaska, California, Oregon, and Washington in 1918.

Buyers and refiners reported purchases of 433 ounces of domestic crude platinum, valued at $39,403.

Incomplete returns from placer mines producing platinum indicate that the production in 1918 was at least 647 ounces of crude platinum. The output in 1918 of 647 ounces compares with the production of 605 ounces in 1917. The miners received from $54 to $98 an ounce for their crude platinum in 1918, the average price being about $91 as compared with $90 for 1917.

Reports received from refiners of platinum, gold bullion, nickel, and copper indicate that 59,753 troy ounces of refined new metals of the platinum group were recovered in 1918, of which about 10,693 troy ounces are believed to be of domestic origin.

Dealers and refiners reported sales in 1918 of 45,583 ounces of secondary platinum metals derived from refining scrap and sweeps. The figures that make up this total probably represent some duplication, as the same metal may be handled as scrap several times in a year.

PLATINUM AND ALLIED METALS IMPORTED FOR CONSUMPTION IN THE UNITED STATES, 1917 AND 1918

METAL	1917		1918	
	Quantity (Troy Ounces)	Value	Quantity (Troy Ounces)	Value
Platinum or crude platinum and unmanufactured products, ingots, bars, sheets, wires	30,207	$2,408,188	54,863	$4,949,855
Platinum, manufactured products, vases, retorts, etc.	(1)	1,347	(1)	8,597
Iridium	3,619	378,678	1,126	126,282
Osmiridium	259	25,456	427	46,321
Osmium	400	23,359	....	......
Palladium	1,239	117,192	240	36,853
	35,724	2,954,220	56,656	5,167,908

(1) Quantity not given.

AVERAGE PRICE PER TROY OUNCE OF REFINED METALS OF THE PLATINUM GROUP, 1917–1918

METAL	1917	1918
Platinum	$103	$105
Iridium	150	175
Iridosmine	80	90
Palladium	110	135

Pottery in 1918. J. MIDDLETON. Separate from Mineral Resources of the United States, 1918, Part II. 15 pp. Issued November 12, 1919.

The value of all domestic pottery marketed in 1918 was $65,222,951 an increase of $9,060,429, or 16 per cent, over the value in 1917. The increase in 1917 over 1916 was $7,945,280, or 16 per cent. The value in 1918 was the greatest recorded by the pottery industry in the United States. It was $27,230,576, or nearly 72 per cent, greater than that of 1913, more than twice as great as that of any year prior to 1910, and more than six times as great as in 1897. Pottery imports increased very slightly, and the ratio of production to consumption, 93 per cent, was the highest recorded.

Every variety of ware as classified in this report, except red earthenware, and sanitary ware, increased in value as compared with 1917, and all except these two attained their maximum values. White ware, which includes the commoner grades of household wares, showed the largest increase, $4,385,457, or 21 per cent; porcelain electrical supplies, the only pottery product used directly in military and naval field operations, increased $3,054,384, or 32 per cent; and china, the pottery of highest grade, increased $1,501,443, or 31 per cent. The value of china in 1918 was four times as great as it was in 1908, a fact which, even allowing for inflated values, augurs well for the future of the pottery industry. Red earthenware decreased in value $158,324, or 15 per cent, and sanitary ware decreased in value $1,395,079, or 11 per cent. One of the causes assigned for the decrease in red earthenware was the curtailment by the Fuel Administration of fuel to florists, who are large users of flower-pots.

Chemical pottery—that is, chemical porcelain and chemical stoneware—was reported from eight states, the same number as in 1917. Indiana and Michigan reported none for 1918, and Iowa and Tennessee entered the list of producers. Chemical porcelain valued at $221,931, an increase of $54,412 over 1917, was reported from only two states in 1918—Colorado and Ohio. New Jersey was the leading state in value of chemical pottery, as in 1917, by a small margin, and Ohio was second. New Jersey's output was valued at $745,741, an increase of $273,060, or 58 per cent, and Ohio's output was valued at $714,456, an increase greater even than that of New Jersey, $285,007, or 66 per cent. These two states reported nearly 83 per cent of the total. Eighteen operators reported chemical pottery—a decrease of one.

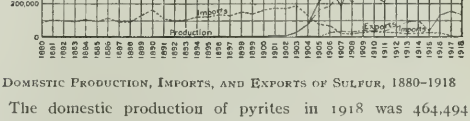
Sulfur and Pyrites in 1918. P. S. SMITH. Separate from Mineral Resources of the United States, 1918, Part II. 20 pp. Issued December 11, 1919.

Through the courtesy of the sulfur producers, it is possible to publish statistics showing the production of sulfur in the United States not only for 1918 but also for 1915, 1916, and 1917, the information for which has not heretofore been published:

SULFUR PRODUCED IN THE UNITED STATES, 1915–1918

	Long Tons
1915	520,582
1916	649,683
1917	1,134,412
1918	1,353,525

The effect of the war on the production of sulfur as well as the changes in the importance of the industry is perhaps best shown by the graphic representation of the production from 1880 to 1918 in the figure.



DOMESTIC PRODUCTION, IMPORTS, AND EXPORTS OF SULFUR, 1880–1918

The domestic production of pyrites in 1918 was 464,494 long tons, valued at $2,644,515, an increase of less than 2,000 long tons in quantity but an increase in value of nearly $160,000 as compared with the production in 1917. The consumption of pyritic ores—that is, the domestic production plus imports—amounted to about 960,000 long tons and was even less than the imports in 1917, or nearly 500,000 tons less than the consumption in that year.

Bibliography of North American Geology for 1918 with Subject Index. J. M. NICKLES. Bulletin 698. 148 pp.

The Analysis of Silicate and Carbonate Rocks. W. F. HILLEBRAND. Bulletin 700 (a revised and enlarged edition of Bulletin 422). 285 pp.

Sodium and Sodium Compounds in 1918. R. C. WELLS. Separate from Mineral Resources of the United States, 1918, Part II. 40 pp. Issued October 24, 1919.

A very comprehensive review of each compound is included.

SODIUM AND SODIUM COMPOUNDS PRODUCED IN THE UNITED STATES IN 1917 AND 1918

	1917		1918	
	Quantity (Short Tons)	Value	Quantity (Short Tons)	Value
Sodium (metal)	(1)	(1)	264	$153,437
Sodium acetate	1,049	$225,828	2,622	460,783
Sodium benzoate	......	......	203	886,058
Sodium bicarbonate	119,177	4,029,499	118,535	3,293,153
Sodium bichromate and sodium chromate	22,446	9,045,133	28,334	9,868,118
Sodium bisulfite and sodium sulfite	13,707	300,668	16,362	478,482
Sodium bromide	......	......	574	438,730
Sodium carbonate:				
Soda ash	1,390,625	38,028,000	1,390,628	35,635,520
Monohydrate and sesquicarbonate	55,035	1,262,875	22,678	482,958
Sal soda	77,939	1,698,520	82,465	2,020,271
Sodium chlorate and sodium perborate	2,915	1,333,426	2,413	1,004,250
Sodium chloride:(2)				
Salt in brine	2,890,588	1,083,586	2,830,600	1,245,265
Rock salt	1,605,025	3,897,595	1,683,941	5,684,661
Evaporated salt	2,482,564	14,959,261	2,724,203	20,010,435
Sodium cyanide, sodium iodide, and sodium peroxide	9,694	6,133,000	9,086	5,427,240
Sodium ferrocyanide	4,173	2,577,667	4,525	2,690,110
Sodium fluoride, acid sodium fluoride, and sodium fluosilicate (silicofluoride)	1,424	397,305	1,228	281,264
Sodium hydroxide (caustic soda)	488,056	29,402,689	513,363	31,854,470
Sodium nitrite	861	480,145	1,701	609,779
Sodium phosphate (including all sodium phosphates)	13,305	711,283	15,620	1,427,947
Sodium silicate	254,011	3,317,547	317,161	5,870,973
Sodium sulfate:				
Salt cake	183,909	2,987,641	141,054	2,844,897
Glauber's salt	47,757	732,403	50,715	1,041,070
Niter cake	387,821	780,278	143,155	595,660
Sodium sulfide	49,494	1,905,473	43,490	2,293,304
Sodium tetraborate (borax)	32,089	4,717,532	26,673	3,909,565
Sodium thiosulfate (hyposulfite	26,598	717,924	26,868	1,051,623
Miscellaneous sodium compounds	4,563	2,062,300	381	1,122,552
	10,164,825	132,787,578	10,198,842	142,682,575

(1) Included in miscellaneous compounds.

(2) R. W Stone, "Salt, Bromine and Calcium Chloride;" U. S. Geol. Survey Mineral Resources for 1918, Part II, pp. 119–121, 1919.

Silica in 1918. F. J. KATZ. Separate from Mineral Resources of the United States, 1918, Part II. 6 pp. Issued December 4, 1919.

SILICA SOLD FOR POTTERY, PAINTS, FILLERS, POLISHERS, ABRASIVES, AND OTHER USES IN 1917 AND 1918

	1917		1918	
MATERIAL	Quantity (Short Tons)	Value	Quantity (Short Tons)	Value
Quartz (vein quartz, pegmatite, and quartzite)	142,673	$318,069	71,740	$259,330
Sand and sandstone[1]	532,454	1,195,142	98,956	620,584
Tripoli	26,069	92,416	19,982	199,854
Diatomaceous earth[2]	3,033	31,368	2,965	24,947
	704,229	1,636,995	193,643	1,104,715

[1] Includes only finely ground material. Figures probably incomplete.

[2] Excludes California product used for filters and as insulating and fireproofing material

So far as can be learned no true flint or chert has been produced for consumption as crushed or ground silica in grinding mills in the United States.

The Department of Commerce records imports of "flint, flints, and flint stones, unground," from several countries. These imports are partly flint pebbles for use in grinding mills and partly material for such uses as are listed in this report. The accurate separation or classification of these materials is impossible. The imports of flint "for consumption" into the United States in 1918 were valued at $135,636, compared with $197,156 in 1917, $313,120 in 1916, $274,904 in 1915, $432,694 in 1914, and $324,662 in 1913. A detailed table of imports of flint pebbles of various kinds and a discussion of domestic substitutes for foreign flint pebbles are given in the chapter on abrasives in Mineral Resources for 1917.

Quartz from quartz veins, pegmatite, and quartzite, amounting to 71,740 short tons and valued at $259,330, was sold in 1918. This was a decrease in quantity of 50 per cent and in value of 18 per cent, as compared with 1917. There was marked decrease in sales of both crude or crushed and ground quartz, and the combined sales of both were less in quantity than has been reported in any year since 1910.

Prices of crude and crushed quartz ranged from $1 to $7.50 a short ton, and, exclusive of large quantities nominally valued at $1 and used in copper smelting, averaged about $3.47 a ton, as compared with $3.25 in 1917, $2.37 in 1916, and $3.30 in 1915. Prices for finely ground, pure quartz commonly ranged from $9 to $18.50 a ton, with exceptional lots selling as high as $40. The average price computed on total sales was $12.80, as compared with $12.25 in 1917, $9.09 in 1916, and $10.56 in 1915.

Quicksilver in 1918. F. L. RANSOME. With a Supplementary Bibliography of I. P. EVANS. Separate from Mineral Resources of the United States, 1918, Part I. 40 pp. Issued October 31, 1919.

QUICKSILVER PRODUCED IN THE UNITED STATES IN 1918

	Ore Treated (Short Tons)	Percentage Tenor Won	Quantity (Flasks of 75 Pounds)	Value
California	355,000[1]	0.24	22,664	$2,663,020
Texas	36,482	0.87	8,451	992,992
Nevada	11,078	0.35	1,044	122,670
Oregon	13,034	0.20	702	82,485
Idaho	60	1.37	22	2,585
	415,654	3.03	32,883	3,863,752

[1] Does not include an unknown quantity of old dump material from which 74 flasks of quicksilver were obtained by concentrating and retorting.

Average price per flask:

San Francisco	$117.50
New York	123.47
London ....Quoted only as	"nominal."
Total number of mines producing	47
Total decrease of production in 1918 from 1917,...flasks	3,276
Total exports from United States (3,098 flasks),....pounds	232,346
Total imports into United States (6,719 flasks),....pounds	503,907

Graphite in 1918. H. G. FERGUSON. Separate from Mineral Resources of the United States, 1918, Part II. 43 pp. Issued October 20, 1919.

Estimates furnished by the producers of crystalline graphite show that out of the total sales of 12,861,839 pounds, 9,811,046 pounds, valued at $1,364,600, or 76 per cent by weight and 94 per cent by value of the total, were flake graphite for the most part suitable for crucible use. The remainder, 3,050,793 pounds, valued at $90,199, was dust or low-grade flake, probably averaging less than 50 per cent of graphitic carbon. The proportion of flake produced was higher than in previous years, owing in part to improved milling methods, and in part to the fact that high freight rates and lack of demand made it unprofitable in many places to save the lower grade graphite of the ore.

The sales of domestic amorphous graphite during 1918 amounted to 6560 short tons, valued at $69,455, as compared with 8301 tons valued at $73,481, in 1917, and 2622 tons, valued at $20,723, in 1916. The increased use of graphite in foundry facings has absorbed the increased output in this country as well as much imported amorphous graphite, chiefly from Mexico. The dust obtained as a by-product in the concentration of flake graphite and the artificial amorphous graphite produced in the electric furnace are competitors of the natural product. Sales of amorphous graphite were reported from four mines in 1918, as against six in 1917. The producing states were Colorado, Nevada, and Rhode Island.

The figures given below represent only the manufactured graphite that comes into competition with natural graphite.

GRAPHITE MANUFACTURED BY THE ACHESON GRAPHITE CO. 1915–1918

	Pounds
1915	5,084,000
1916	8,397,281
1917	10,474,649
1918	9,182,272

Average Prices of Ceylon Graphite c. i. f. New York, 1914–1918
(Cents per pound)

	Lump		Chip		Dust		
	First Grade	Second Grade	First Grade	Second Grade	First Grade	Second Grade	Remarks
1914	6½– 9½	7½– 8½	7¼– 7¾	6½– 7	4¾– 5¼	3½– 4	Low, first half; high, second half
1915	9⅝–20	8 –14	7 –14	6½–12	7½– 9½	6½– 9½	Low, first half; high, second half
1916	20 –28	14 –21	13½–20	11½–17	9½–12	9½–10	Low, first half; high, second half
1917	28 –32	21 –23	20 –23	17 –19	11 –13	10 –12	High level maintained throughout
1918	28½–15¼	22 –14	21½–12½	18½–11	12 –10½	10 – 9	High, first half; low, second half

Estimated Percentages (by Quantity) of Natural Graphite Consumed in the United States for Various Purposes

	Per cent
Crucibles	45
Foundry facings	25
Lubricants	10
Pencils and paints	5
Stove polish	5–10
All other uses	10– 5

Gypsum in 1918. R. W. Stone. Separate from Mineral Resources of the United States, 1918, Part II. 17 pp. Issued November 6, 1919.

Nearly 24 per cent less gypsum was mined in the United States in 1918 than in 1917, owing to a reduction in building operations. The output was less than that in any year since 1909, and the great reduction may be ascribed wholly to the war. On the other hand, the total value of the crude and calcined gypsum produced in 1918 surpassed that of any other year.

Sand and Gravel in 1918. R. W. Stone. Separate from Mineral Resources of the United States, 1918, Part II. 17 pp. Issued October 31, 1919.

A total of 2,172,887 short tons of glass sand was produced in the United States in 1918, an increase of 12 per cent over the output in 1917. The average price in 1918 was $1.94 a ton, an increase of 40 per cent over price in 1917.

During 1918 the steel mills of the country were busy on war orders and a large number of foundries of metals were working at top speed. There was an increase of 5 per cent in the production of molding sand over that of 1917, and the price per ton received averaged 13 per cent higher. The output was 4,910,178 short tons, valued at $5,121,865, as compared with 4,660,968 tons valued at $4,303,809, in 1917.

Filter sand is clean silica sand in sorted sizes used for beds in water filtration plants and in small mechanical filters. In 1918 the output was 51,111 short tons, valued at $74,977, an average price of $1.47 a ton, as compared with 62,170 short tons, valued at $47,351, or 76 cents a ton, in 1917.

The man in the street might regard as a joke the statement that sand is used as an ingredient of some fertilizers; nevertheless, in 1918 New York and Pennsylvania reported that 31,110 short tons of sand, valued at $22,360, were used as filler for fertilizer.

A few tons of fine-grained high-grade silica sand is sold annually for use by blacksmiths in welding iron and soft steel. Sand for this purpose is put up in 25-pound sacks and so brings a high price per ton. Likewise, high-grade silica sand, because of its whiteness, is sold in 3 and 5 pound cartons for use in mechanical toys and thus retails at about $60 a ton.

A few hundred tons of clean, even-grained, and high-grade silica sand are sold annually in small lots for use as a standard in physical tests of other sands.

Fluorspar and Cryolite in 1918. E. F. Burchard. Separate from Mineral Resources of the United States, 1918, Part II. 13 pp. Issued December 9, 1919.

The total quantity of domestic fluorspar reported to the Survey as sold (shipped from mines) in 1918 was 263,817 short tons, valued at $5,465,481, compared with 218,828 tons, valued at $2,287,722, in 1917, an increase in quantity of nearly 21 per cent, and in value of 139 per cent. The general average price per ton f. o. b. mines or shipping points for all grades of spar in 1918, according to these figures, was $20.72, compared with $10.45 in 1917.

As usual, gravel spar, the grade used principally for flux in the manufacture of open-hearth steel, constituted the bulk of the output. The shipments of gravel spar in 1918 amounted to 236,121 short tons, valued at $4,735,260, compared with 183,144 tons, valued at $1,759,920, in 1917, an increase in quantity of 29 per cent, and in total value of 169 per cent. The sales of lump spar in 1918 were 18,944 short tons, valued at $457,018, compared with 25,548 tons, valued at $349,460, in 1917, a decrease in quantity of 6,604 tons, or 26 per cent, but an increase in value of $107,558, or 31 per cent. Ground spar was marketed in 1918 to the extent of 8752 short tons, valued at $273,203, compared with 10,136 tons, valued at $178,342, in 1917, a decrease in quantity of 1384 tons, or 14 per cent, but an increase in value of $94,861, or 53 per cent.

The total quantity of crude fluorspar mined cannot be ascertained exactly. From such figures as are available it is apparent that the crude spar mined in 1918 amounted to 326,039 short tons, compared with 280,825 tons in 1917, an increase of 16 per cent. The quantity of merchantable spar mined in 1918 amounted to 270,412 short tons.

Fluorspar suitable for optical purposes has occasionally been found in mines in southern Illinois, western Kentucky, and some western states. During 1918, 371 ounces of optical fluorspar were produced from material mined in Riverside County, Cal., and Crittenden County, Ky.

The entire supply of natural cryolite used in the United States is imported from Greenland. Some artificial cryolite is understood to be produced in the manufacture of aluminum, but no statistics are available as to its output.

The quantity of cryolite reported to have been imported duty free for consumption in the United States in 1918 was 1950 long tons, valued at $97,500, compared with 4383 tons, valued at $218,500, in 1917. The average value per ton at the Greenland port of shipment was $50 in 1918, compared with $49.86 in 1917.

BUREAU OF MINES

Ninth Annual Report of the Director of the Bureau of Mines to the Secretary of the Interior for Fiscal Year Ended June 30, 1919. 120 pp. Paper, 15 cents. Issued October 1919.

Experiment Stations of the Bureau of Mines. V. H. Manning. Bulletin 175. 106 pp. Paper, 25 cents. Issued August 1919.

BUREAU OF STANDARDS

Coking of Illinois Coal in Koppers Type Oven. An Operating Test at the St. Paul Plant of Minnesota By-Products Coke Company Conducted Jointly by National Bureau of Standards and Bureau of Mines. R. S. McBride and W. A. Selvig. Technologic Paper 137. 51 pp. Paper, 10 cents. Issued November 17, 1919. For this test, approximately 7600 tons of coal from the Orient mine of the Chicago, Wilmington and Franklin Coal Co., which operates in Franklin County, Ill., were obtained. This coal was handled in the plant of the Minnesota By-Product Coke Co., at St. Paul, Minn., which plant operated for the entire period of the test on this coal alone. All phases of coal handling, oven operation, by-product recovery, and laboratory tests were under observation by a staff of government representatives. Altogether 37 engineers and chemists were employed for this work, and in addition the Bureau of Standards and the Bureau of Mines had the benefit of advice and comment from a considerable number of expert engineers who are specialists in the field of coke-oven operation. The quantity of all products was carefully weighed or measured at regular intervals, samples of each of the products were taken, and complete analyses of the coal and these products have been made. Altogether, therefore, this report covers complete observations on all parts of the plant for the entire period from September 27 to October 5, 1918.

Oxygen Content by the Ledebur Method of Acid Bessemer Steels Deoxidized in Various Ways. J. R. Cain and E. Pettijohn. Scientific Paper 346. 12 pp. Paper, 5 cents. Issued November 11, 1919.

1—The Ledebur method for oxygen did not indicate significant differences in oxygen content in steels with nearly identical chemical composition and heat treatment but having different deoxidation treatments.

2—No differences in nitride nitrogen were shown for such steels.

3—The work of Boylston cited in this paper showed no distinctive differences in the gas content of such steels as obtained by heating *in vacuo* to 1000° for 30 hrs.

4—Judged by the evidence of this paper and that of Boylston, the three chemical methods just named—being those much used heretofore—are inadequate for the study of deoxidation.

5—Mechanical tests show some differences in quality of the steels according to deoxidation treatment, but these differences are not marked and are masked somewhat by other factors.

Heat Treatment of Duralumin. P. D. Merica, R. G. Waltenberg and H. Scott. Scientific Paper 347. 46 pp. Paper, 10 cents. Issued November 15, 1919.

The heat treatment of alloys of the type duralumin was investigated and the effect observed of variations in the heat-treating conditions, such as quenching temperature, temperature of quenching bath, and of aging or tempering, and time of aging upon the mechanical properties.

Conclusions are drawn relative to the best conditions for commercial heat treating practice for this alloy. The temperature of quenching should not be above that of the $CuAl_2$, aluminum eutectic, which is usually about 520° C., but should be as near to this as possible without danger of eutectic melting. The pieces should be held at this temperature from 10 to 20 min. and quenched preferably in boiling water. The hardening may for most purposes best be produced by aging for about 5 days at 100° C.

A theory of the mechanism of hardening of duralumin during aging, after quenching from higher temperatures, was developed, which is based upon the decreasing solubility of the compound $CuAl_2$ in solid solution in aluminum with decreasing temperatures from 520° C. to ordinary temperatures. It is believed that the precipitation of excess $CuAl_2$ which is suppressed by quenching proceeds during aging, the precipitation taking place in very highly dispersed form. The hardening is due to the formation of this highly dispersed precipitate.

According to this theory the hardening of duralumin during aging or tempering after quenching presents a very close analogy with that of steel, and the evidence in support of the theory is of the same nature and of approximately the same competence as that in support of the prevailing theory of the hardening of steel.

Equilibrium Conditions in the System Carbon–Iron Oxide–Hydrogen in Relation to the Ledebur Method for Determining Oxygen in Steel. J. R. Cain and L. Adler. Scientific Paper 350. 14 pp. Paper, 5 cents. Issued November 10, 1919.

Annual Report of the Director of the Bureau of Standards to the Secretary of Commerce for the Fiscal Year Ended June 30, 1919. Miscellaneous Publication 40. 293 pp.

Electrolytic Resistance Method for Determining Carbon in Steel. J. R. Cain and L. C. Maxwell. Technologic Paper 141. 21 pp. Paper, 5 cents. Issued December 6, 1919.

The purpose of this study was to investigate the accuracy, speed, and practicability of a method for determining carbon in steel, dependent in principle on passing the carbon dioxide produced by direct combustion of the metal into a solution of barium hydroxide of known electrical resistance. After complete absorption of this gas the resistance is again determined, and from the increase (due to precipitation of barium ions) the percentage of carbon is deduced.

Cadmium Electrode for Storage Battery Testing. H. D. Holler and J. M. Braham. Technologic Paper 146. 15 pp. Paper, 5 cents. Issued December 12, 1919.

Tests of Eighteen Concrete Columns Reinforced with Cast Iron. J. Tucker, Jr., and J. G. Bragg. Technologic Paper 122. 38 pp. Paper, 10 cents. Issued November 14, 1919.

DEPARTMENT OF AGRICULTURE

General Regulations Governing Importation, Manufacture, Storage, and Distribution of Fertilizers and Fertilizer Ingredients, Promulgated by the President of United States under Authority Conferred on Him by Act Approved August 10, 1917, to provide further for national security and defense by encouraging production, conserving supply, and controlling distribution of food products and fuel. Circular 145. Paper, 5 cents. Issued November 7, 1919.

Articles from the Journal of Agricultural Research

Notes on the Composition of the Sorghum Plant. J. J. Willaman, R. M. West, D. O. Spriestersbach and G. E. Holm. 18 (October 1, 1919), 1–33.

Simple Method for Measuring the Acidity of Cereal Products, Its Application to Sulfured and Unsulfured Oats. V. Birckner. 18 (October 1, 1919), 33–49.

Rate of Absorption of Soil Constituents at Successive Stages of Plant Growth. J. S. Burd. 18 (October 15, 1919), 51–73.

Relation of the Concentration and Reaction of the Nutrient Medium to the Growth and Absorption of the Plant. D. R. Hoagland. 18 (October 15, 1919), 73–117.

Natural Carbonates of Calcium and Magnesium in Relation to the Chemical Composition, Bacterial Contents, and Crop-Producing Power of Two Very Acid Soils. S. D. Conner and H. A. Noyes. 18 (November 1, 1919), 119–127.

Effect of Variation in Moisture Content on the Water-Extractable Matter of Soils. J. C. Martin and A. W. Christie. 18 (November 1, 1919), 139–145.

Pathology of Dourine with Special Reference to Microscopic Changes in Nerve Tissues and Other Structures. R. J. Formad. 18 (November 1, 1919), 145–155.

Do Mold Spores Contain Enzymes? F. M. Coerper. 18 (November 15, 1919), 179–195.

Nitrogen Metabolism of Two-Year-Old Steers. S. Bull and H. S. Grindley. 18 (December 1, 1919), 241–255.

Response of Citrus Seedlings in Water Cultures to Salts and Organic Extracts. J. F. Breazeale. 18 (December 1, 1919), 267–275.

Losses of Organic Matter in Making Brown and Black Alfalfa. C. W. Swanson, L. E. Call and S. C. Salmon. 18 (December 15, 1919), 299–305.

Sunflower Silage. R. E. Neidig and L. E. Vance. 18 (December 15, 1919), 325–329.

Effect of Oxidation of Sulfur in Soils on the Solubility of Rock Phosphate and on Nitrification. O. M. Shedd. 18 (December 15, 1919), 329–345.

BOOK REVIEWS

Commercial Laboratory Notes. Vol. I. By C. L. Petty. Publication of the Dayton Metal Products Company, Research Division, Dayton, Ohio. Thompson Printing Co., Dayton, Ohio, 1919. Price, $6.00.

An analytical method has little chance of maintaining its identity when once turned loose upon the world. The author in his preface says that "these methods as a whole are the ones in daily use by the Pennsylvania Railroad Co., at Altoona, Pa., with some slight additions, subtractions, and modifications." This blanket acknowledgment identifies the source of many of the methods, *viz.*, the specifications of the Pennsylvania Railroad Co., but it does not identify the particular methods and the changes which they might have undergone. The methods as issued by the P. R. R. served as standards for producer and consumer, but with additions, subtractions, and modifications this can no longer be said.

The field covered is wide, including the analysis of non-ferrous alloys, steels, iron, paint, oils, rubber, cement, soaps, etc. As a whole the methods are satisfactory for commercial laboratories, and especially those which originated and have been tested by the Pennsylvania Railroad laboratory. There is, however, an unevenness which is striking. One-half page is devoted to the analysis of chromium and vanadium in steel, while five and one-half pages are given to the simple Williams method for manganese. Again, in the gravimetric determination of phosphorus in bronze nearly half a page is given to an explanation of the simple calculation of results; in the bismuthate method for manganese in steel involving reactions between permanganic acid and sodium arsenite solutions nothing is said of calculation of results. Under the chapter heading "Methods of Sampling and Analysis" one might expect a discussion of sampling in general, but we find the heading refers to soap only; under the chapter "Titre Test" we did not find a method for determining free, fatty acids but a method for determining the melting points of the acids. In some cases the methods have been edited; in others not at all, but in spite of the unevenness the book will be useful to workers in the commercial field.

The book is mounted in a loose leaf binder which adds enormously to the expense, and increases the liability to loss or misplacement of individual pages.

Henry Fay

The Hydrogenation of Oils. By Carleton Ellis, S.B. 2nd Ed. xvii + 767 pp. 240 illustrations. D. Van Nostrand Co., New York City, 1919. Price, $7.50.

In this second edition the author has adopted the same method of treatment as in the first edition, that is to say, the book is, in effect, an annotated bibliography of the subject rather than a systematic setting forth of the chemical, mechanical, and commercial principles which underlie the manufacturing art and determine the financial returns. The book, however, is much more than a bibliography, because in it the writers and inventors whose work is referred to are made to tell, largely in their own words, the story of their aims and ideas, copious extracts from the literature and patents forming a large part of the volume.

The work has been brought in this way well up to date, and the present edition comprises 767 pages as against 340 pages in the first edition. An account of the recent litigation between Procter & Gamble and the Berlin Mills Company upon the Burchenal Patent No. 1,135,351 for a food product is included in Appendix B. In such a work it is almost unavoidable that the chemistry and mechanics contained in it should be distributed over a considerable mass of reading material, and one rather misses in studying the book such a condensed discussion of the present state of the principles and practice as might, perhaps, with advantage have been added. In other words, the result is rather a compendious and elaborate account of what the patentees and writers upon the subject have to say than a discussion of the present state of the art. The book certainly fills a distinct need, and is of great assistance to those interested in the business of hydrogenation, whether from the manufacturing or from the legal standpoint, but its very fulness emphasizes the need at the present time for the preparation of a work in which all these various plans and ideas might be analyzed and weighed and the respective merits of different processes and designs of machinery compared one with another as to their practical value so that the progress of manufacture might be materially assisted.

P. C. McIlhiney

Liquid Fuel for Internal Combustion Engines. By Harold Moore, M.Sc. Tech., F.C.S. xv + 200 pp. 49 illustrations. D. Van Nostrand Co., New York City, 1918. Price, $5.00.

The author discusses in a concise manner the various chemical differences between liquid fuels. For an adequate understanding of their properties, a similarly short description is also given of the various forms of internal combustion engines.

The book will be found helpful to chemists who desire a brief description of the different types of oil-using engines and also to the engineer who needs a brief and more or less elementary discussion of the chemical characteristics of the different liquid fuels. The information is reliable, well arranged and up-to-date, a considerable part resulting directly from the author's own experience.

One unfortunate point is to be noted. On page 10, in discussing the distillation products obtained from petroleum, the statement is made that "The first important fuel is *benzene*, which distills between 70 and 120° C." Doubtless the word here intended is *benzine* and the error is one of orthography. However, it is unfortunate to revive this word, now practically obsolete, as a term for designating a light petroleum distillate, especially since benz*ene* is prescribed as the proper termination for the hydrocarbon C_6H_6 in preference to benzol, presumably obsolete since the war.

S. W. Parr

Dyeing with Coal-Tar Dyestuffs. By C. M. Whittaker, B.Sc. 214 pp. D. Van Nostrand Co., New York City, 1919. Price, $3.00.

The author has given in a comparatively condensed volume the methods employed and the essential principles involved in the application of the coal-tar dyes to all classes of textile fibers. To avoid complications only typical examples of each class of dyes are used to illustrate the procedures, except now and then certain dyes which are characterized by some outstanding property. The irregularities which may arise during various dyeing processes are not overlooked and many valuable suggestions are made as to corrective measures.

A section is devoted to the vegetable and mineral dyes, and another to the miscellaneous uses of dyes—such as calico printing, lake and paint manufacture, soap coloring, typewriter ribbons, inks, food coloring, indicators, and medicinal uses. The closing section deals with the valuation and detection of dyestuffs.

In general, the volume confines itself to the properties and uses, and does not deal at all with composition or manufacture. No attempt is made to describe the numerous types of machines used in dyeing.

The author's special training as a color chemist not only renders the volume authoritative, but leads now and then to the introduction of valuable observations from his long experience. This volume should prove of value both to the student and to the experienced color chemist.

Louis A. Olney

NEW PUBLICATIONS

By Clara M Guppy, Librarian, Mellon Institute of Industrial Research, Pittsburgh

Alloy Steels: Manufacture and Uses of Alloy Steels. H. D. Hibbard. 12mo. 96 pp. Price, $1.25. John Wiley & Sons, Inc., New York.

Asbestos: From Mine to Finished Product. Asbestos and Mineral Corporation. 8vo. 194 pp. Asbestos and Mineral Corporation, New York.

Butter: Practical Butter-Making. A Treatise for Butter-Makers and Students. C. W. Walker-Tisdale and T. R. Robinson. 143 pp. Price, 5s. 6d. Headley Brothers, London.

Carburetors: Metering Characteristics of Carburetors. National Advisory Committee for Aëronautics. *Bulletin* 49. 55 pp. Government Printing Office, Washington, D. C.

Catalysis in Theory and Practice. E. K. Rideal and H. S. Taylor. 8vo. 496 pp. Price, $6.00. The Macmillan Co., New York.

Chemical Industry: L'Industrie Chimique aux Etats-Unis. Charles Mayer. 291 pp. Price, 6fr. Dunod, Paris.

Chemistry: Les Progres de la Chimie en 1918. Traduction Française Autorisée des "Annual Reports on Progress of Chemistry for 1918." André Kling, Editor. 322 pp. Price, 15fr. Gauthier-Villars & Cie, Paris.

Chemistry and Its Mysteries: The Story of What Things Are Made of Told in Simple Language. C. R. Gibson. 12mo. 246 pp. Price, $1.50. J. B. Lippincott Co., Philadelphia.

Color Chemistry: Grundlegende Operationen der Farbenchemie. H. E. Fierz. 323 pp. Schulthess & Co., Zurich.

Dyeing with Coal-Tar Dyestuffs. C. M. Whittaker. 214 pp. D. Van Nostrand Co., New York. (See Book Reviews, this issue.)

Industrial Gases. H. C. Greenwood. 371 pp. Price, 12s. 6d. Baillière, Tindall & Cox, London.

Industrial Good Will. J. R. Commons. 8vo. 214 pp. Price, $2.00. McGraw-Hill Book Co., New York.

Minerals: Strategy of Minerals. A Study of the Mineral Factor in the World Position of America in War and in Peace. G. O. Smith, Editor. 372 pp. Price, $2.50. D. Appleton & Co, New York.

Organic Chemistry: Notions Fondamentales de Chimie Organique. Charles Moureu. 6th Ed. 8vo. 552 pp. Price, 24fr. Gauthier-Villars & Cie, Paris.

Organic Compounds: Preparation of Organic Compounds. E. De Barry Barnett. Price, 10s. 6d. J. & A. Churchill, London.

Petroleum Handbook: A Practical Reference Book. S. O. Andros. 16mo. 200 pp. Price, $2 00. Shaw Pub. Co., Chicago.

Pyrometry: Special Pyrometry Volume. Includes Papers Given at Symposium on Pyrometry at Chicago Meeting of the American Institute of Mining and Metallurgical Engineers, September 1919. 750 pp. Price before publication, $5.00. Later, $6.00. American Institute of Mining and Metallurgical Engineers, New York.

Solubilities of Inorganic and Organic Compounds: A Compilation of Quantitative Solubility Data from the Periodical Literature. Atherton Seidell. 2nd Ed. Enlarged and revised. 8vo. 843 pp. Price, $7.50. D. Van Nostrand Co., New York.

Technical Dictionary: Illustrated Technical Dictionary in Six Languages, English, German, French, Russian, Italian, Spanish. Kurt Deinhardt and Alfred Schlomann, Editors. 12 vol. G. E. Stechert & Co., New York.

RECENT JOURNAL ARTICLES

Alloy Steels: Progress in Metallurgy of Alloy Steels. H. F. Wood. *The American Drop Forger*, Vol. 6 (1920), No. 1, pp. 25–27.

Ammonium Sulfate: Manufacture of Ammonium Sulfate from Gypsum. D. H. B. Wride. *The Chemical Age (London)*, Vol. 2 (1920), No. 30, pp. 32–33.

Anilines: The Estimation of Aniline in Commercial Anilines. W. J. Sanderson and W. J. Jones. *Journal of the Society of Chemical Industry*, Vol. 39 (1920), No. 1, p. 8*t*.

Coke: Moisture in Blast-Furnace Coke. W. H. George. *Journal of the Society of Chemical Industry*, Vol. 38 (1919), No. 22, pp. 394*t*–396*t*.

Colloid Chemistry and Its Application in the Arts. J. V. Meighs. *Chemical Age*, Vol. 2 (1920), No. 1, pp. 325–329.

Copper: Production of Copper from Secondary Material. Methods of Sampling Miscellaneous Products Entering the Refinery. Lawrence Addicks. *Chemical and Metallurgical Engineering*, Vol. 22 (1920), No. 3, pp. 119–122.

Dyeing: General Review and Bibliography of Dyeing. P. E. King. *Color Trade Journal*, Vol. 5 (1919), No. 6, pp. 164–169; Vol. 6 (1920), No. 1, pp. 18–23.

Dyestuffs: Nomenclature of Dyestuffs. J. M. Matthews. *Color Trade Journal*, Vol. 6 (1920), No. 1, pp. 29–31.

Ethyl Alcohol from Wood. F. W. Kressman. *Chemical Age*, Vol. 2 (1920), No. 1, pp. 319–321.

Ethyl Chloride: The Technical Applications of Ethyl Chloride. Albert Hemming. *Journal of the Society of Chemical Industry*, Vol. 39 (1920), No. 1, pp. 1*t*–8*t*

Glass Industry: The American Glass Industry. E. E. Sullivan. *The Chemical Engineer*, Vol. 27 (1919), No. 11, pp. 281–283.

Iron and Steel Literature for 1919, Review of. A Classified List of the More Important Books, Serials and Trade Publications during the Year; with a Few of Earlier Date not Previously Announced. E. H. McClelland. *Blast Furnace and Steel Plant*, Vol. 8 (1920), No. 1 pp. 8–10.

Lampblack, By-Product from Oil Gas Manufacture, a Readily Marketed Domestic Fuel. E. L. Hall. *American Gas Engineering Journal*, Vol. 112 (1920). No. 5, pp. 77–80

Metals: Les Métaux Résistants aux Acides. C. Matignon. *Chimie et Industrie*, Vol. 2 (1919), No. 11–12, pp. 1283–1302.

Nitrogen Interest in 1919. E. B. Maxted. *The Chemical Age (London)*, Vol. 2 (1920), No. 29, pp. 6–8.

Paper: Coloring of Paper. Otto Kress. *Paper*, Vol. 25 (1920), No. 18, pp. 17–23; No. 19, pp. 17–20; No. 20. pp. 21–23.

Petroleum: Crude Petroleum Industry in 1919. J. D. Northrop. *Engineering and Mining Journal*, Vol. 109 (1920), No. 3, pp. 129–133.

Platinum in 1919. J. M. Hill. *Engineering and Mining Journal*, Vol. 109 (1920), No. 3, pp. 112–113.

Porcelain: The Story of Chemical Porcelain. H. S. Coors. *The Chemical Engineer*, Vol. 27 (1919), No. 11, pp. 277–279

Potash in America: The Concluding Part of a Review of the Industry. A. E. Wells. *The Chemical Engineer*, Vol. 27 (1919), No. 11, pp. 283–284.

***p*-Phenylenediamine.** T. Callan and J. A. R. Henderson. *Journal of the Society of Chemical Industry*, Vol. 38 (1919), No. 24, pp 408*t*–410*t*.

Proteins: Notes on the Evolution of Proteins. E. L. Kennaway. *Chemical News*, Vol. 120 (1920), No. 3117, pp. 13–16.

Pyrite: Some Chemical Data on Coal Pyrite; a Study of the Use of Coal Pyrite for the Manufacture of Sulfuric Acid. H. F. Yancey *Chemical and Metallurgical Engineering*, Vol. 22 (1920), No. 3, pp. 105–109.

Pyrometry in the Blast Furnace Plant. P. H. Royster and T. L. Joseph. *The Blast Furnace and Steel Plant*, Vol. 7 (1919), No. 11, pp. 556–560.

Refractories: 1919 Sees Improvements in Refractories. R. M. Howe. *The American Drop Forger*, Vol. 6 (1920), No. 1, pp. 43–44. Same in *Blast Furnace and Steel Plant*, Vol. 8 (1920), No. 1, pp. 59–60.

Refractories in Heat Treating Furnaces; in Which the Author Gives a Classification of Different Types of Refractory Materials. J. A. King. *The American Drop Forger*, Vol. 6 (1920), No. 1. pp. 44–48.

Selenium: General Applications of Selenium; Its Utilization in Biological Chemistry and in the Glass and Rubber Industries. Louis Ancell. *Scientific American Monthly*, Vol. 1 (1920), No. 1, pp. 28–29.

Silver in 1919. S. R. Wagel. *Engineering and Mining Journal*, Vol. 109 (1920), No. 3, pp. 109–111.

Soap Manufacture: Colloidal Clay in Soap Manufacture. F. E. Weston. *The Chemical Age (London)*, Vol. 2 (1920), No. 31, pp. 58–60.

Spiegeleisen: Use of Spiegeleisen in Steel Manufacture. H. D Hibbard. *Chemical and Metallurgical Engineering*, Vol. 22 (1920). No. 5, pp. 209–210

Sulfates: Estimation of Sulfates in the Presence of Organic Sulfonic Acids. T. Callan, J. A. R. Henderson, and R. Barton. *Journal of the Society of Chemical Industry*, Vol. 38 (1919), No 24, pp. 410*t*–411*t*.

Sulfite Alcohol: A Short Bibliography of Sulfite Alcohol. A List of Articles on the Production of Alcohol from Sulfite Waste Liquors. C. J West. *Paper*, Vol. 25 (1919), No. 13, pp. 19–20, 23.

Synthetic Cast Iron: A Continuous Process of Rapid Carburization during Melting of Steel Turnings. C. A. Keller. *Chemical and Metallurgical Engineering*, Vol. 22 (1920), No. 2 pp. 83–88.

Tannin: Report on Tannin. W. H Krug. *Journal of the American Leather Chemists' Association*. Vol. 15 (1920), No. 1 pp. 2–11.

Tannins: Report on Tannins. J. H. Yocum. *Journal of the American Leather Chemists' Association*, Vol. 15 (1920), No. 1, pp 13–21.

Vitamines: Their Influence on Human Nutrition. E. B Forbes. *Chemical Age*, Vol. 2 (1920), No 1, pp 348–350.

MARKET REPORT—FEBRUARY, 1920

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

		Feb. 1	Feb. 15
Acid, Boric, cryst., bbls.	lb.	.15	.15
Hydrochloric, com'l, 22°	lb.	.02	.02
Hydriodic	oz.	.19	.19
Nitric, 40°	lb.	.07	.07
Phosphoric, 50% tech.	lb.	.24	.24
Sulfuric, C. P.	lb.	.08	.08
Chamber, 66°	ton	22.00	22.00
Oleum	ton	27.00	27.00
Alum, ammonia, lump	lb.	.04	.04
Aluminum Sulfate (iron-free)	lb.	.03	.03
Ammonium Carbonate, pwd.	lb.	.13	.13
Ammonium Chloride, gran.	lb.	.15	.15
Ammonia Water, carboys, 26°	lb.	.10	.10
Arsenic, white	lb.	.11½	.12
Barium Chloride	ton	150.00	150.00
Nitrate	lb.	.11	.11
Barytes, white	ton	25.00	25.00
Bleaching Powd., 35%, Works	100 lbs.	2.75	3.00
Borax, cryst., bbls.	lb.	.09½	.09½
Bromine, tech., bulk	lb.	.60	.60
Calcium Chloride, fused	ton	21.00	21.00
Chalk, precipitated	lb.	.05½	.05½
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	8.00	8.00
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.50	1.50
Iodine, resublimed	lb.	4.10	4.10
Lead Acetate, white crystals	lb.	.14	.14
Nitrate	lb.	.15	.15
Red American	100 lbs.	.10½	.10½
White American	100 lbs.	.09½	.09½
Lime Acetate	100 lbs.	2.00	2.00
Lithium Carbonate	lb.	1.50	1.50
Magnesium Carbonate, powd.	lb.	.19	.19
Magnesite	ton	65.00	65.00
Mercury flask	75 lbs.	85.00	80.00
Phosphorus, yellow	lb.	.35	.35
Plaster of Paris	100 lbs.	1.50	1.50
Potassium Bichromate	lb.	.30	.30
Bromide	lb.	.85	.85
Carbonate, calc., 80–85%	lb.	.24	.24
Chlorate, cryst.	lb.	.15	.15
Cyanide, bulk, 98–99%	lb.	.30	.30
Hydroxide, 88–92%	lb.	.30	.32
Iodide, bulk	lb.	3.35	3.10
Nitrate	lb.	.14	.14
Permanganate, U. S. P.	lb.	.70	.70
Salt Cake	ton	17.00	17.00
Silver Nitrate	oz.	.82½	.82½
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	2.25	2.40
Caustic, 76%	100 lbs.	4.25	4.50
Sodium Acetate	lb.	.25	.25
Bicarbonate	100 lbs.	2.25	2.25
Bichromate	lb.	.22	.22
Chlorate	lb.	.10	.10
Cyanide	lb.	.25	.25
Fluoride, technical	lb.	.15	.15
Hyposulfite	100 lbs.	3.60	3.60
Nitrate, 95%	100 lbs.	3.25	3.35
Silicate, 40°	lb.	.02	.02
Sulfide	lb.	.05	.05
Bisulfite powdered	lb.	.05	.05
Strontium Nitrate	lb.	.23	.23
Sulfur, flowers	100 lbs.	3.75	3.75
Crude	long ton	30.00	30.00
Talc, American, white	ton	20.00	20.00
Tin Bichloride	lb.	.21½	.21½
Oxide	lb.	.60	.60
Zinc Chloride, U. S. P.	lb.	.50	.50
Oxide, bbls.	lb.	.22	.22

ORGANIC CHEMICALS

		Feb. 1	Feb. 15
Acetanilid	lb.	.60	.60
Acid, Acetic, 28 p. c.	100 lbs.	3.75	3.75
Glacial	lb.	.12	.12½
Acetylsalicylic	lb.	1.00	1.00
Benzoic, U. S. P., ex-toluol	lb.	.80	.80
Carbolic, cryst., U. S. P., drs.	lb.	.15	.15
50- to 110-lb. tins	lb.	.21	.21
Acid (*Concluded*)			
Citric, crystals, bbls.	lb.	1.15	1.07
Oxalic, cryst., bbls.	lb.	.40	.40
Pyrogallic, resublimed	lb.	2.50	2.50
Salicylic, bulk, U. S. P.	lb.	.55	.55
Tartaric, crystals, U. S. P.	lb.	.70	.70
Trichloracetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.14	.14
Alcohol, denatured, 190 proof	gal.	.80	.80
Ethyl, 190 proof	gal.	5.25	5.25
Wood, 95%	gal.	2.00	2.00
Amyl Acetate	gal.	3.65	3.65
Camphor	lb.	3.40	3.40
Carbon Bisulfide	lb.	.06	.06
Tetrachloride	lb.	.11	.11
Chloroform, U. S. P.	lb.	.30	.30
Creosote, U. S. P.	lb.	.85	.75
Cresol, U. S. P.	lb.	.17	.17
Dextrine, corn	lb.	.07	.07
Imported Potato	lb.	.17	.17
Ether, U. S. P., conc., 100 lbs	lb.	.17	.19
Formaldehyde	lb.	.45	.43
Glycerin, dynamite, drums	lb.	.25	.25
Starch, corn	100 lbs.	5.35	5.35
Potato, Jap.	lb.	.08½	.08½
Rice	lb.	.25	.25
Sago	lb.	.05	.05

OILS, WAXES, ETC.

		Feb. 1	Feb. 15
Beeswax, pure, white	lb.	.70	.70
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	.19	.18
Ceresin, yellow	lb.	.14	.14
Corn Oil, crude	lb.	.19	.19
Cottonseed Oil, crude, f. o. b. mill	lb.	.19½	.19½
Menhaden Oil, crude (southern)	gal.	.95	.95
Neat's-foot Oil, 20°	gal.	2.25	2.25
Paraffin, 128–130 m. p., ref.	lb.	.11½	.11½
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs.	bbl.	19.35	19.35
Rosin Oil, first run	lb.	.97	.97
Shellac, T. N.	lb.	1.70	1.70
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.95	1.95
Stearic Acid, double-pressed	lb.	.28½	.28½
Tallow Oil, acidless	gal.	1.55	1.55
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	2.04	2.04

METALS

		Feb. 1	Feb. 15
Aluminum, No. 1, ingots	lb.	.31½	.31½
Antimony, ordinary	100 lbs.	9.87	9.87
Bismuth	lb.	2.52	2.52
Copper, electrolytic	lb.	.19½	.19½
Lake	lb.	.19	.19
Lead, N. Y.	lb.	.09	.09
Nickel, electrolytic	lb.	.45	.45
Platinum, refined, soft	oz.	160.00	160.00
Silver	oz.	1.35	1.35
Tin	lb.	.60	.60
Tungsten Wolframite	per unit	7.00	7.00
Zinc, N. Y.	100 lbs.	9.75	9.75

FERTILIZER MATERIALS

		Feb. 1	Feb. 15
Ammonium Sulfate	100 lbs.	7.50	7.50
Blood, dried, f. o. b. N. Y.	unit	7.50	7.50
Bone, 3 and 50, ground, raw	ton	48.00	48.00
Calcium Cyanamide, unit of Ammonia		4.50	4.50
Fish Scrap, domestic, dried, f. o. b. works	unit	7.25	7.25
Phosphate Rock, f. o. b. mine:			
Florida pebble, 68%	ton	Nom.	Nom.
Tennessee, 78–80%	ton	11.00	11.00
Potassium muriate, 80%	ton	240.00	240.00
Pyrites, furnace size, imported	unit	.18	.18
Tankage, high-grade, f. o. b. Chicago	unit	8.00	8.00

COAL-TAR CHEMICALS

Crudes

		Feb. 1	Feb. 15
Benzol, C. P.	gal.	.34	.30
Cresol, U. S. P.	lb.	.16	.16
Naphthalene, flake	lb.	.08	.08
Phenol, drums	lb.	.15	.15
Toluol, 90%	gal.	.28	.28
Xylol, water white	gal.	.40	.40

Intermediates

		Feb. 1	Feb. 15
Acids:			
Anthranilic	lb.	4.00	4.00
Benzoic	lb.	.80	.80
Broenner's	lb.	1.75	1.75
Cleves	lb.	2.00	2.00
Cresylic, 95%	gal.	.90	.95
F	lb.	3.00	3.00
Gamma	lb.	2.50	2.50
H	lb.	1.70	1.70
Metanilic	lb.	1.70	1.70
Monosulfonic	lb.	.15	.15
Napthionic, crude	lb.	.65	.65
Neville & Winther's	lb.	1.75	1.85
Phthalic	lb.	.60	.60
Picric	lb.	.25	.25
Sulfanilic	lb.	.35	.35
Tobias'	lb.	2.25	2.25
Amido Azo Benzol	lb.	1.15	1.15
Aniline Oil	lb.	.34	.35
For Red	lb.	.65	.65
Aniline Salt	lb.	.44	.44
Anthracene, 80%	lb.	.65	.65
Anthraquinone	lb.	5.00	5.00
Benzaldehyde, tech.	lb.	.75	.75
U. S. P.	lb.	1.50	1.50
Benzidene Base	lb.	1.25	1.40
Benzidine Sulfate	lb.	1.10	1.15
Diamidophenol	lb.	6.00	6.00
Dianisidine	lb.	10.00	10.00
p-Dichlorbenzol	lb.	.10	.10
Diethylaniline	lb.	1.40	1.40
Dimethylaniline	lb.	1.10	1.10
Dinitrobenzol	lb.	.30	.31
Dinitrotoluol	lb.	.38	.38
Diphenylamine	lb.	.65	.65
G Salt	lb.	.65	.65
Hydroquinone	lb.	2.00	2.00
Metol	lb.	11.50	11.50
Monochlorbenzol	lb.	.09	.09
Monoethylaniline	lb.	2.15	2.15
a-Naphthylamine	lb.	.40	.40
b-Naphthylamine	lb.	1.15	1.15
b-Naphthol, crude	lb.	.55	.55
m-Nitraniline	lb.	1.00	1.00
p-Nitraniline	lb.	1.25	1.30
o-Nitrobenzol, crude	lb.	.16	.16
Rectified (Oil Myrbane)	lb.	.18	.18
p-Nitrophenol	lb.	.80	.80
p-Nitrosodimethylaniline	lb.	1.90	1.90
o-Nitrotoluol	lb.	.17	.17
p-Nitrotoluol	lb.	1.15	1.15
m-Phenylenediamine	lb.	1.10	1.10
p-Phenylenediamine	lb.	2.35	2.20
Phthalic Anhydride	lb.	.60	.60
Primuline Base	lb.	3.00	3.00
R Salt	lb.	.65	.70
Resorcin, tech.	lb.	3.75	4.00
U. S. P.	lb.	6.00	6.00
Schaeffer Salt	lb.	.65	.75
Sodium Naphthionate	lb.	1.10	1.10
Thiocarbanilid	lb.	.60	.60
Tolidine, Base	lb.	1.65	1.70
Toluidine, mixed	lb.	.44	.44
o-Toluidine	lb.	.25	.28
m-Toluylenediamine	lb.	1.35	1.35
p-Toluidine	lb.	1.75	1.75
Xylidene, crude	lb.	.50	.50

COAL-TAR COLORS

Acid Colors

		Feb. 1	Feb. 15
Black	lb.	1.15	1.15
Blue	lb.	3.00	3.00

Acid Colors (*Continued*)

		Feb. 1	Feb. 15
Fuchsin	lb.	2.50	2.50
Orange III	lb.	1.00	1.00
Red	lb.	1.10	1.10
Violet 10B	lb.	6.50	6.50
Alkali Blue, domestic	lb.	4.75	4.75
Imported	lb.	8.00	8.00
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	2.00	2.00
Erythrosine	lb.	12.00	12.00
Indigotine, conc.	lb.	3.00	3.00
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.50	1.50
Ponceau	lb.	1.00	1.00
Scarlet 2R	lb.	1.00	1.00

Direct Colors

		Feb. 1	Feb. 15
Black	lb.	.95	.95
Blue	lb.	1.10	1.10
Brown	lb.	1.55	1.55
Fast Red	lb.	3.50	3.50
Yellow	lb.	2.00	2.00
Violet, con't	lb.	2.20	2.20
Chrysophenine, domestic	lb.	2.50	2.50
Imported	lb.	3.80	3.80
Congo Red, 4B Type	lb.	1.60	1.60
Primuline, domestic	lb.	3.00	3.00

Oil Colors

		Feb. 1	Feb. 15
Black	lb.	.70	.70
Blue	lb.	1.65	1.65
Orange	lb.	1.40	1.40
Red III	lb.	1.65	1.65
Scarlet	lb.	1.75	1.75
Yellow	lb.	1.70	1.70
Nigrosine Oil, solution	lb.	.90	.90

Sulfur Colors

		Feb. 1	Feb. 15
Black	lb.	.30	.30
Blue, domestic	lb.	.80	.80
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.90	.90

Chrome Colors

		Feb. 1	Feb. 15
Alizarin Blue, bright	lb.	7.75	7.75
Alizarin Red, W. S. Paste	lb.	5.00	5.00
Alizarin Yellow R	lb.	1.50	1.50
Chrome Black, domestic	lb.	1.25	1.25
Imported	lb.	2.20	2.20
Chrome Blue	lb.	2.50	2.50
Chrome Green, domestic	lb.	1.50	1.50
Chrome Red	lb.	2.00	2.00

Basic Colors

		Feb. 1	Feb. 15
Auramine, O, domestic	lb.	3.25	3.25
Auromine, OO, imported	lb.	4.25	4.25
Bismarck Brown Y	lb.	.90	.90
Bismarck Brown R	lb.	1.20	1.20
Chrysoidine R	lb.	1.00	1.00
Chrysoidine Y	lb.	.90	.90
Green Crystals, Brilliant	lb.	6.00	6.00
Indigo, 20 p. c. paste	lb.	.75	.75
Fuchsine Crystals, domestic	lb.	4.00	4.00
Imported	lb.	12.00	12.00
Magenta Acid, domestic	lb.	4.25	4.25
Magenta Crystals, imported	lb.	10.00	10.00
Malachite Green, crystals	lb.	4.50	4.50
Methylene Blue, tech	lb.	2.25	2.25
Methyl Violet	lb.	2.60	2.60
Nigrosine, spts. sol.	lb.	.85	.85
Water sol., blue	lb.	.65	.65
Jet	lb	.90	.90
Phosphine G., domestic	lb.	7.00	7.00
Rhodamine B ex-con't	lb.	27.00	27.00
Victoria Blue, base, domestic	lb.	6.00	6.00
Victoria Green	lb.	6.00	6.00
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY
AT ESCHENBACH PRINTING COMPANY, EASTON, PA.

Volume XII APRIL 1, 1920 No. 4

Editor: CHARLES H. HERTY
Assistant Editor: LOIS W. WOODFORD
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Published monthly. Subscription price to non-members of the American Chemical Society, $6.00 yearly; single copy, 60 cents
Price per single copy to American Chemical Society members, 50 cents. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted
Entered as Second-class Matter December 19, 1908, at the Post Office at Easton, Pa., under the Act of March 3, 1879
Acceptance for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized July 13, 1918

All communications should be sent to The Journal of Industrial and Engineering Chemistry
Telephone: Vanderbilt 1930 **Cable Address: Jiechem** **35 East 41st Street, New York City**
Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Secretary, 1709 G Street, N. W., Washington, D. C.

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EDITORIALS

RELIEF FOR THE PATENT OFFICE

On March 5, 1920, the Nolan Bill, H. R. 11984, which will give to the Patent Office resources for the enlargement and improvement of its personnel and general office operations, was passed by the House of Representatives.

This relief legislation embraces the general features which were urged by the Patent Committee of the American Chemical Society, whose chairman, Mr. E. J. Prindle, has worked indefatigably. For a while there seemed to be difficulty in getting the attention of Congress, but the hearings held before the Rules Committee of the House proved to be an eye opener. The bill went through the Houes without a roll call, and is now with the Senate Committee on Patents, Senator George W. Norris, chairman. It is very important that Senator Norris and senators in general should know how strongly chemists favor this bill and the pressing importance of its speedy passage. Letters from individual chemists to their senators and to the chairman would go far toward arousing interest in the bill. This seems to be the only thing needed to assure its passage. It will be a fortunate day for the American chemical industry when the Patent Office is enabled to accomplish more adequately the purpose for which it was founded.

THE CHEMICAL WARFARE SERVICE

The Army Reorganization Bill passed the House of Representatives on March 18, 1920. It contains a section providing for the Chemical Warfare Service as a separate unit of the Army, with a chief holding the rank of brigadier general, and with 90 officers, ranging from colonel to second lieutenant, and 1500 enlisted men. It was in the House that friends of the Chemical Warfare Service had most to fear, for certain members had been outspoken in their opposition to the Service being made a separate unit. This opposition, however, gave way, and now the bill goes to the Senate, where it seems there is absolute unanimity of sentiment that the Chemical Warfare Service shall not only be a separate unit, but that full provision shall be made for its complete development and thorough efficiency. It is a safe prediction that any changes made in the section pertaining to the Chemical Warfare Service from now on will be only such as tend to strengthen and improve the Service.

The unexpected announcement of the transfer of Major General William L. Sibert from the head of the Chemical Warfare Service to the command of Camp Gordon, Atlanta, Ga., was a distinct shock to all who had been connected with this new branch of our military system. Whatever may have been the reasons which led to this transfer, one thing is certain: As he leaves that Service which he so aggressively developed, General Sibert carries with him not only the high personal esteem but also the genuine affection of all who now are or who were during the strenuous days previous to the armistice members of the Chemical Warfare Service. Moreover, while this transfer removes him from the Washington atmosphere, nevertheless the clear, logical, and forceful testimony which he gave before committees of both the House and Senate made such an impression as to ensure the success of his ideas with the Congress, and this we take it is perhaps the greatest service General Sibert has performed, for he has done that which will safeguard in large measure the future peace of this country.

It is indeed fortunate that as a successor to General Sibert Lt. Col. Amos A. Fries was available. His fine service in the A. E. F. and the work he has done for the Chemical Warfare Service since his return give assurance that the active leadership of the Service in the future could not have been placed in stronger or wiser hands. Colonel Fries, whom we hope soon to hail as Brigadier General Fries, can count upon the whole-hearted and enthusiastic support of the civilian chemists of the country.

"NOTHING TO EAT BUT FOOD"

We have just received Bulletin No. 1 of the Free Trade League, among whose members are noticed the names of prominent citizens. The bulletin is directed against the bills designed to protect the tungsten, magnesite, zinc, pearl buttons, scientific instruments, and coal-tar products industries.

The chief wail of the Free Trade League is that great secrecy has shrouded the introduction and progress of these bills. Secrecy, indeed! When we think of the journeyings to Washington of all parties affected by these bills, when we think of the groaning of the Government Printing Office under the mass of testimony presented at public hearings on the bills, the charge of lack of openness reminds us of the plaint of the man who sang:

> Nothing to eat but food,
> Nothing to breathe but air,
> Nothing to wear but clothes and shoes
> And a hat on the top of my hair

We don't imagine Bulletin No. 1 will have much influence on public thought or on congressional action, but we wonder how the members of the League square the term "secret movement," etc., with legislation which has on two separate occasions been urged by the President in his messages to Congress, which passed the House of Representatives after a full week of debate, and which now has enthusiastic non-partisan support in the Senate.

The Free Trade League is a little late in getting into the game, but it is very amusing to note the combined opposition of the American Protective Tariff League and the Free Trade League to the bill to make permanent the coal-tar chemical industry. The former describes the bill as a "grab;" the latter says it was "concocted by interests." A strange pair of bedfellows that!

AIR-CASTLES

The complexities of present day rates of foreign exchange lead to rather unexpected developments. For instance, the editor of a well-known German techno-chemical journal turns a deaf ear to the opinions frequently expressed in this country that this is no time for foreign loans. With that sublime confidence which frequently during the past few years has been so utterly out of place, he writes to an American chemist, known to him only through his subscription list and through a contributed article some seven or eight years ago. Without the slightest suggestion of security other than that of Teutonic good faith, he baldly requests a loan of five hundred dollars, not because of necessity, but avowedly because of the opportunity which the present rate on the mark as compared with the dollar offers, confident of course that at the end of the three-year period for which he requests the loan there will be a considerable increase in the value of the mark.

This five hundred dollars would represent at present about fifty thousand marks. If the exchange went back to normal, he could return two thousand marks, leaving him a profit of some forty-eight thousand marks, or twelve thousand dollars. It is not difficult to picture the air-castles that can be constructed on the basis of such rosy visions; the only difficulty, we learn from our correspondent, is that the loan will not be made, nor the letter even answered. We mention it here in the thought that possibly this may not be the only letter of its kind floating around the country. The wily doctor may have used a mimeograph. What next?

NOTES

It's at St. Louis and the date is April 12th.

We had the good fortune recently to visit one of the large research laboratories connected with the new dye industry. An interesting sidelight of that tour of inspection was the great number of American-made optical instruments and thermometers in use, to the unexcelled character of which the chemists freely testified. The Bacharach bill makes sure the permanency of the American scientific instruments industry.

The letter of retiring Secretary Lane to the President proved one of the striking events of the month. Mr. Lane paid a generous compliment to the chemists of America in the following words:

> It is not generally known that the largest society of scientists in the world is the American Chemical Society. If as appears now to be the promise, the immediate future is to be largely in the hands of the chemists, America need not look forward too sparingly, for we have a stock of men of this training which no other nation can excel.

The Sixth National Exposition of Chemical Industries will be held at the Grand Central Palace, New York City, in the week of Sept. 20, 1920. The management has issued a printed list of those exhibitors who have already engaged space. There are 308 names on the list, and the date is six months distant. Clearly the Sixth Exposition is to be a record breaker.

The way to begin is to begin. The matter of recovering the lost ground referred to in our last issue has already begun. President Mark W. Potter of the C. C. & O. Railway writes us that this road proposes to continue the utilization of the chemist and that steps are already under way to reopen their chemical survey laboratories. He writes:

> It is our thought to be more progressive in the future. * * * The function of the chemical engineer is of increasing importance. In the future more than in the past, successful achievement will mean the discovery of new opportunities, the increase of efficiency and elimination of waste, and in all the work that is ahead of us the chemical engineer must be of increasing importance.

Senator Moses (New Hampshire) seeks to amend the coal-tar chemical bill by removing the embargo feature and making it a straight tariff measure. In the *Daily News Record* of March 17, 1920, the Senator is quoted thus: "There can be no question as to who is behind my bill." Sure, that's an easy guess, the earmarks are perfectly plain. And by that same token there can be no question that the Senator's amendment is in no wise to be considered as an effort to safeguard or develop the American industry, but is simply an expression of the willingness of "who is behind my bill" to pay 20 per cent extra for the privilege of getting all the German dyes they want. Of course there are all sorts of ways of recouping that 20 per cent. It's a pretty safe guess, too, that every dye importer is loud in his praises of the Senator's amendment. Sure, they know the game. Maybe they are circularizing the mills again in order to assist Congress in its deliberations.

A correspondent suggests a useful form of coöperation between universities and industries: the establishment of prizes, in the chemistry departments of universities having adequate library facilities, for the best bibliographies compiled by students on subjects assigned by the industry. It is believed that the industry would be a two-fold gainer from such an investment, directly, in the value of the bibliographies compiled, and indirectly, through the better training in handling chemical literature which the competing students would receive.

Dr. William H. Walker, Director of the Division of Industrial Coöperation and Research at the Massachusetts Institute of Technology, contributes, page 394, this issue, an interesting discussion and explanation of the "Technology Plan" which was utilized so effectively in raising the $8,000,000 endowment fund. The matter has aroused widespread interest and it is felt that the same plan in more or less modified form can and doubtless will be used by many other institutions. Cornell University has already adopted a very similar form of plan and contract. It will be interesting to note modifications and possible improvements as the thought of the educational and industrial world is brought to bear upon this plan, and equally interesting to note the outworking of the plan at Technology under the vigorous administration which it will without doubt receive from Dr. Walker.

ORIGINAL PAPERS

PREPARATION OF NITROGEN AND HYDROGEN MIXTURE BY DECOMPOSITION OF AMMONIA[1]

By R. O. E. Davis and L. B. Olmstead

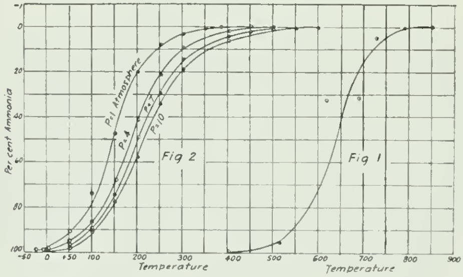
Bureau of Soils, Department of Agriculture, Washington, D. C.

Received October 2, 1919

In work in the Bureau of Soils laboratory on the synthesis of ammonia done in coöperation with the Nitrate Division of the War Department, it was necessary to obtain a mixture of hydrogen and nitrogen in the ratio of $3H_2$ to N_2 in amounts of several hundred cubic feet per day. This gas should be free from impurities, especially carbon monoxide and oxygen. Anhydrous ammonia being easily obtained, it was decided to build an electric furnace to decompose it and use the decomposed gases as the required mixture of nitrogen and hydrogen.

HISTORICAL

Investigations on the decomposition of ammonia were made in 1884 by Ramsay and Young[2] at temperatures of 500° C. and 830° C. They found that decomposition began under most favorable circumstances slightly below 500° C. Though decomposition occurred below 500° C. the rate of reaction was too slow to observe in the time of the test. The tests were made in tubes of porcelain and iron with pieces of broken porcelain as catalyst. Decomposition was found to be one and a half to two times greater in an iron tube than in a porcelain one.



The curve in Fig. 1 shows the quantities of ammonia found in the iron tube starting with pure ammonia. Decomposition was complete only at about 780° C. Haber[3] found that the velocity of reaction when $t = 700°$ C. was still so small that equilibrium could not be established with certainty. Plank[4] discusses the theoretical values at one to 10 atmosphere pressures. These values are shown in the curves of Fig. 2. These theoretical equilibria would exist only after months or years as the velocity of reaction is very slow.

Perman and Atkinson[5] made tests between $t = 677°$ C. and 1111° C. with a reaction vessel of porcelain. Mercury, platinum, and iron as catalysts were all found to accelerate the reaction.

Bodenstein and Kranendiech[1] operated between 790° C. and 880° C. using quartz glass for catalyzer and reaction vessel. Their results verify those of other investigations. From their experiments it is shown clearly that iron acts as a catalyzer toward this reaction in both directions.

DESCRIPTION OF FURNACE

The furnace devised by us for carrying out this reaction is shown in Fig. 3.

A diagrammatic sketch of the furnace shows the outer tube *a* to be a piece of 5-in. standard wrought iron pipe 4 ft. long closed at the ends with flanges *c*, and the upper 34 in. wound with nichrome ribbon, *k*. Inside this pipe is a piece, *b*, of 2.5-in. standard iron pipe, 35 in. long, wound with nichrome wire, *k*. A pyrometer tube, *n*, extends 14 in. into the upper end of this inner pipe and the vacant space *f* (about $^1/_4$ cu. ft.) is filled with the catalyst (in this case iron turnings or steel wool). Automobile spark plugs were adapted to carry the leads through the flanges. The lower portion is the heat interchanger *g* which actually consists of three coils of $^1/_8$ in. pipe connected in parallel. The anhydrous ammonia enters the interchanger through the lower flange, passes upward over the interchanger coils, through the catalyst between the heaters, then passes down through the catalyst inside the inner pipe, through the interchanger coils, and emerges as a mixture of $3H_2$, N_2, and NH_3, the percentage of NH_3 depending upon the temperature and rate of flow. The gases are passed through a water scrubbing tower to remove the remaining ammonia and then through a meter to the gas holder. The ammonia remaining in the scrubbed gases rarely exceeded 0.2 per cent and quite often is nil.

It will be seen that the inner heater is very favorably situated since it operates in a reducing atmosphere. It consumes about 65 per cent and the outer coil about 35 per cent of the total energy. The source of current is a 25 cycle, 40 volt transformer. It was originally intended to use copper turnings as a catalyst and the furnace was wound inductively. With iron as catalyst the power factor is reduced to 92 per cent. The coils are connected so that their magnetic fluxes are opposed. The maximum power consumption at 40 volts is 2 k. v. a. which is inadequate to maintain the furnace at the proper temperature for a flow of ammonia as great as the catalyst can decompose. In a new furnace of similar design, the length is increased one foot and the diameter one inch. The inner coil is wound non-inductively on 3.5-in. cold drawn boiler tube and has a carrying capacity of 4 k. v. a. at 40 volts. The outer coil is also wound non-inductively with a maximum capacity of 3 k. v. a. The voltage is adjusted so that the inner coil will dissipate about 80 per cent of the energy. The capacity of the heat interchanger is considerably increased, and the inlet and outlet gases travel through about 10 ft. of double pipe in countercurrent flow. Fine steel wool is used for catalyst.

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[1] Published by permission of Chief of Ordnance.

[2] *J. Chem. Soc.*, **45** (1884), 88.

[3] *Z. Electrochem.*, **40**, 2144.

[4] *Z. ges. Kolt-Industrie*, March and May 1915, p. 8; reviewed in *Am. Soc. Refrig. Eng. J.*, **2** (1915), 34.

[5] *Proc. Roy. Soc. London*, **74** (1905), 110.

[1] *Festschrift, W. Nernst* (1912), pub. by Knapp, Halle; *Chem. Abs.*, **7** (1913), 1647.

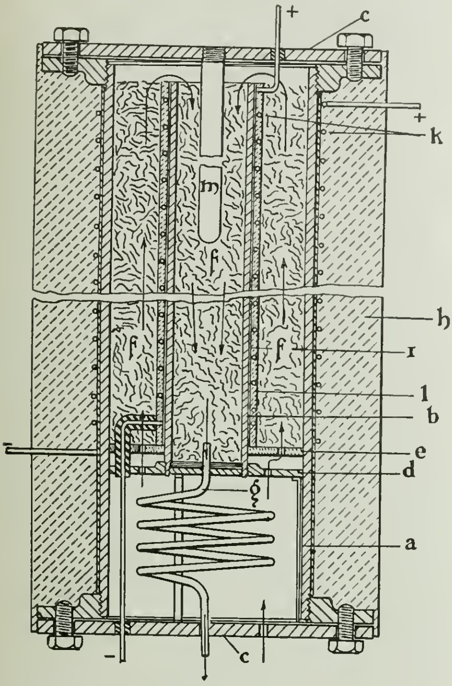

FIG. 3—FURNACE FOR THE DECOMPOSITION OF AMMONIA

a—5-in. iron pipe	*g*—heat interchange coil
b—2.5-in. iron pipe	*h*—insulating material
c—flange ends	*i*—alundum sheath
d—flange end to inner pipe	*k*—resistance coil of chromel wire
e—perforated asbestos board	*l*—alundum cement
f—catalyst space	*m*—pyrometer well

The weight of the furnace is partially supported from above to prevent deformation and the sides and top are covered with 7 in. of infusorial earth.

RESULTS

Table I shows some results obtained in the furnace using iron shavings as catalyst. The flow is measured by the decomposed gas free from NH_3 which passes through the meter.

TABLE I—DECOMPOSITION OF AMMONIA
(Catalyst: Iron. Space: 0.22 Cu. Ft.)

Temp. ° C.	Flow Cu. Ft. per Min.	Decomposition Per cent
370	0.01	73.0
470	0.15	84.0
540	0.01	94.0
600	0.20	97.0
600	2.00	94.5
610	0.50	93.5
650	0.62	99.6
650	1.50	97.4
675	0.50	99.7
675	1.00	99.5
700	1.50	99.7
710	2.00	99.6
735	0.82	99.7

For ordinary operation a temperature of 675° C. is maintained which enables one to obtain about 100 cu. ft. per hr. of the hydrogen-nitrogen gas mixture with a power consumption of 2 k. v. a. with loss of 0.3 to 0.4 per cent of ammonia. The equilibrium of a system of H_2–N_2–NH_3 at that temperature and atmospheric pressure theoretically should be about 0.02 per cent NH_3. The average time of contact in the catalyst space is about 5 sec. This time could probably be reduced considerably.

A small preliminary furnace in which copper chips and turnings were used for catalyst was employed before this one was constructed. Table II shows results obtained with this.

TABLE II—DECOMPOSITION OF AMMONIA
(Catalyst: Copper. Space: 0.11 Cu. Ft.)

Temp. ° C.	Flow Cu. Ft. per Min.	Decomposition Per cent
750	0.01	96.0
750	0.25	75.0
800	0.05	97.3
850	0.01	99.7
850	0.22	99.4
850	0.95	90.5
900	0.85	96.2
925	0.50	99.3
925	1.00	97.5

It will be seen that copper requires a temperature about 200° C. higher than iron, and a longer contact. The figures are not strictly comparable for the iron surface was probably of the order of ten times that of the copper. Beilby and Henderson[1] emphasize the fact that ammonia decomposes less rapidly in contact with copper than with iron.

Because of the lower operating temperature and cheapness, iron was chosen in preference to copper as a catalyst.

The furnace with steel shavings was in operation for about 6 mo. when the outer coil burned out. On taking apart the iron, shavings were found to have sintered into a compact mass and to be attached firmly to the sides of the iron pipe. The pipe itself, which had operated continuously in an atmosphere of hydrogen and nitrogen, showed attack from within to such a degree that it was granular and cracked about two-thirds the distance through the wall (0.25 in. thick) and crystallized the other third. The metal was very brittle and the pipe was readily broken up with a hammer. Beilby and Henderson[2] and Henderson and Galletly[3] found a similar deterioration of metals exposed to ammonia at high temperatures. Probably this was due to the formation of iron nitride or hydride, or both. The nichrome wire used as resistance winding seemed to be in as good condition as when first wound. The maximum temperature to which the furnace had been subjected was not over 900° C., and this temperature was reached inadvertently and maintained for a very short time.

THE ACTION OF CERTAIN ORGANIC ACCELERATORS IN THE VULCANIZATION OF RUBBER[4]

By G. D. Kratz, A. H. Flower and Cole Coolidge

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Since the introduction of the use of organic substances to assist in, or to accelerate, the vulcanization of rubber, there has been remarkably little added to the literature upon the subject. Furthermore, what has been written has been confined largely to reviews of a general nature. Although King,[1] Peachey,[2] Twiss,[3] Spence,[4] and others[5] have contributed to this subject, the majority of investigators have remained reticent, despite the fact that the patent files are replete with information.

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[1] *J. Chem. Soc.*, **79** (1901), 1245.

[2] *Loc. cit.*

[3] *J. Soc. Chem. Ind.*, **27** (1908), 387.

[4] Presented before the Rubber Division at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

The present paper records a portion of the results procured in an attempt to obtain further information in regard to the action of certain organic substances in accelerating the vulcanization reaction. Throughout this work we have chosen to employ only substances which have previously been cited by others and whose definite chemical composition permits comparison with homologs or other closely related compounds. The activities of the substances from a practical standpoint were considered of secondary importance. Further, while we most assuredly recognize that the vulcanization reaction is, essentially, a catalytic one, we have chosen to employ the term "accelerator" rather than "catalyst," when referring to the organic substances in question. This distinction is deemed necessary to avoid misunderstanding, and to discriminate between catalysis as it is generally understood and as it must be applied to the vulcanization of rubber. In this regard, it is necessary to take into consideration the fact that a large number of the organic substances used to accelerate the vulcanization of rubber decompose below the temperatures at which vulcanization is ordinarily effected, and that many of them show a tendency to combine with the sulfur under vulcanizing conditions. Again, as most of the rubber mixtures in actual use contain mineral substances, the possibility of a reaction of these substances with the organic accelerators involving the alteration or decomposition of the latter, is far from remote. In fact, even before the general use of synthetic organic substances as accelerators, Esch[6] found it necessary to employ calcium and magnesium oxides with certain albuminous bodies in order to obtain the desired results. Likewise, Peachey[7] has noted a marked increase in the activity of *p*-nitrosodimethylaniline when used in conjunction with magnesia. Litharge was found to diminish the effectiveness of this accelerator.

Although we are confident that the use of organic substances as accelerators was practiced in the factories of this country long before the first patent on the subject was taken out abroad, the predominance of the early patents was undoubtedly German. In fact, the latter people, with their thoroughness and the realization of the possibilities in the subject, attempted to restrict the use of all nitrogenous substances by the use of such generalities as are found in one of Bayer and Company's patents.[1] That few, if any, applications for license to use these patents were made during the war is an indication of our priority in this field.

The first German patents upon accelerators appeared almost coincidentally with certain patents for the preparation of synthetic rubber, when it was found that this substance was abnormally slow in its reaction with sulfur. In this connection, Bayer and Company found that piperidine or its homologs[2] and the piperidine salt of piperidyl-dithiocarbamic acid[3] effected a marked acceleration in the vulcanization of Kondakow's rubber,[4] and, subsequently, they extended their claims to cover natural rubber. Prior to the above Bayer patents, however, a patent was issued to Wo. and Walther Ostwald[5] for the treatment of rubber, gutta-percha, and the like, with pyridine, quinoline, dimethylaniline, etc., in order to prevent its becoming hard and fragile. It is most remarkable that in the course of this work the Ostwalds failed to note the action of certain salts of these and other closely related substances in accelerating the vulcanization of the rubber, even though the parent substances themselves possess little, if any, action.

Immediately following the patents for the use of piperidine and its derivatives appeared a variety of specifications covering the use of dimethylamine,[6] aldehyde ammonia, tetra- and hexamethylenediamines, *p*-phenylenediamine, and naphthylenediamines;[7] the formaldehyde condensation products of aniline and its homologs;[8] the guanidines;[9] naphthylamine;[10] and a large number of other amino-compounds, or nitrogenous substances, all of which have been mentioned previously by King, Peachey, Twiss, Spence, or Ditmar, and include such substances as quinoline and its salts, the quaternary ammonium bases, urea and thiourea derivatives, and a host of others. In their patents, Bayer and Company cover the urea and thiourea derivatives of saturated aliphatic amines, both open and closed carbon chains, which are saturated methylene open-carbon chain bases. The term "methylene base" is held to be generic to those bases which are saturated bases as distinguished from unsaturated bases as aniline. Suffice to say, that both aniline and diphenylthiourea were employed in this country long before the appearance of any of the above specifications.[11]

Although not specified in some of the foregoing patents, many of these were drawn upon the assumption that the activities of the various substances depended largely upon their nitrogenous nature and the basicity of the substances in question.

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[1] *Met. & Chem. Eng.*, **15** (1916), 231; **18** (1918), 246.

[2] *India Rubber J.*, **52** (1916), 603; *J. Soc. Chem. Ind.*, **36** (1917), 321; **36** (1917), 424, 950.

[3] *J. Soc. Chem. Ind.*, **36** (1917), 782.

[4] THIS JOURNAL, **10** (1918), 115.

[5] *Gummi Ztg.*, **29** (1915), 425; **30** (1916), 303; *India Rubber World*, **56** (1917), 190; *Caoutchouc et gutta-percha*, **15** (1918), 9637; *Rubber Age*, **3** (1918), 78.

[6] D. R. P. 273,482 (1912).

[7] *J. Soc Chem. Ind.*, **36** (1917), 424

[1] D. R P. 280,198 (1914).

[2] D. R. P. 255,680, 266,618 (1912); 268,387, 265,221 (1912).

[3] D. R. P. 266,619 (1912); U. S. Patent 1,126,469 (1915).

[4] *J. prakt. Chem.*, **64** (1901), 109.

[5] D. R. P. 221,310 (1908).

[6] D R. P. 269,512; French Patent 464,533.

[7] D. R. P. 280,198 (1914); U. S. Patent 1,149,580 (1915).

[8] British Patent 7,370 (1914).

[9] British Patent 17,760 (1916).

[10] U. S. Patent 1,296,469 (1919).

[11] In this connection it is interesting to note that in this country attention was directed to the use of urea as an accelerator before the appearance of these or any other patents upon urea or the thioureas. This is said to have been the result of observations made upon certain African rubbers, reputed to have been coagulated with human urine, and which were found to vulcanize with more than average rapidity.

In view of the well-known effect of such inorganic bases as caustic soda or potash upon the vulcanization of rubber, the opinion that the basicity of certain substances is closely connected with their action as accelerators has found quite a few adherents. Among these is Twiss,[1] who believes that both the organic and inorganic accelerators, all of basic nature, exert their influence in a similar manner. According to Twiss, the more powerful action of the organic bases is due to their greater solubility in the rubber, a principle which he has applied in preparing very active accelerators by the use of an organic liquid which would be soluble in the rubber and also act as a solvent for alkali. In a subsequent patent[2] he has still further extended this view to include such materials as solutions of sodium and potassium in aniline, the action of which would be difficult indeed to classify if essential differences are held to exist between the action of organic and inorganic accelerators. Peachey,[3] however, in his patent upon *p*-nitrosodimethylaniline, has taken another view, and attributes the activity of this substance, primarily, to the presence of the nitroso group. Subsequently, Peachey[4] has also expressed the opinion that, while the dissociation constant of 1×10^{-8}, referred to in the Bayer patents, does actually form a dividing line between accelerating and non-accelerating bases, there are other classes of accelerators (as *p*-nitrosodimethylaniline) which are not basic, or but slightly so. Further, in order to emphasize not only the effect of certain groups, but also the position of these groups in the molecule, Peachey has cited the nitroso bases as powerful accelerators, and pointed out that the isomeric nitrosamines, in which the nitroso group is not in direct combination with the nucleus, are inert.

Likewise, Spence has mentioned that the activity of certain substances which contain groups in the para position are more active than the isomeric substances, in which the groups are in the ortho, or meta position, and has cited the relative activities of *p*-phenetidine and *o*-phenetidine as an example. He has also called attention to the increase effected in the activity of substances as accelerators by the introduction of other groups into the nucleus. As a case in point, he has made reference to the increase in the activity of diphenylthiourea when it is converted into tetramethyldiaminodiphenylthiourea. While there is no doubt that these differences exist as expressed by Peachey and Spence, it is to be regretted that no figures were given by either of them by which the relative activities of the various substances might be recorded.

Our own experience, a portion of which is embodied in the experimental part of this paper, in the main confirms the results of Peachey and Spence; and in fact, in many ways, permits of their amplifications. Not only have we found certain groups, and the position of these groups in the primary nucleus, to have a marked effect upon the activity of the substance under investigation, but we have found that if the effect produced by one or more groups is to be considered on a strictly comparable basis, the size (molecular weight) of the parent substance must also be taken into account. On the other hand, we are equally well convinced that with many substances it is possible to place too great stress upon the presence of certain groups and their position in the nucleus. It would appear that the effect produced by the different groups is largely determined by their behavior and ultimate condition as the original substance undergoes decomposition or chemical change, and that the activity of substances not originally basic is due to their conversion into basic substances during vulcanization.

For example, in our preliminary experiments we found that urea was slightly more active than thiourea. Thiourea, in turn, was more active than monophenylthiourea, and the latter more active than diphenylthiourea. The same was true in the case of the guanidines, both monophenylguanidine and diphenylguanidine being found more active than triphenylguanidine, although the conditions of our experiment did not permit of a differentiation between the two substances first mentioned. In the case of the thiourea, the natural inferences would be that the activity of the parent substance depended largely upon the presence of the NH_2 groups, with a consequent diminution in the effect produced as phenyl replaces hydrogen. In the case of the guanidines, the great difference in activities of mono- and diphenylguanidines, when compared with that of triphenylguanidine, may be attributed to the fact that in the latter substance the phenyl group has replaced imido rather than amido hydrogen.

Again, when we made a comparison between a cyclic monamine and diamine, we found the latter, in accordance with the now general understanding, to be much more active than the former, if the groups are in the para position. On the formation of the anhydro-formaldehyde condensation products of these substances, however, although the activities of each were increased by the substitution of methylene groups for the hydrogen of the amino groups in the original substances, this increase in the case of the monoamine was much less than that produced by the introduction of a second amino group into the original nucleus. Although the two types of compounds are not isomeric, this is in line with Peachey's statement as to the effect produced when groups are introduced into a side-chain rather than the original nucleus.

In our subsequent and more extensive experiments, wherein we employed aniline as a basis of comparison, we found that the replacement of the amino group in aniline by hydroxyl actually decreased the rate of vulcanization to less than that of the control mixture which contained no accelerator. The introduction of a second hydroxyl group in the para position was found to cause a still greater retardation in the rate of reaction. In fact, when allowance was made for the difference in the molecular weights of the two substances, the anti-accelerating effect of hydroquinone was found to be just twice that of phenol. The difference between the effect of one amino group and two amino groups in the para position has already been mentioned, and here again, after having corrected for the molecular weights of the two substances, *p*-phenylenediamine was found to be almost exactly twice as active as aniline. When we employed *p*-amidophenol, however, in order to obtain an amino group and an hydroxyl group in the para position to each other, our results were not strictly in accordance with those of Peachey and Spence, who found that this substance was without action or but mildly active On the contrary, we found *p*-amidophenol to be more active than aniline. The inference from our results would be that although the effect of the (OH) group is that of a retardant, its position in the nucleus, and its subsequent influence upon the decomposition of the nucleus during vulcanization, are of less importance than the effect produced by the stronger and positive (NH_2) group.

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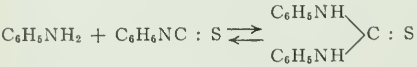
[1] *J. Soc. Chem. Ind.*, **36** (1917), 782; British Patent 110,059 (1916).
[2] British Patent 124,276 (1919).
[3] British Patent 4,263 (1914).
[4] *J. Soc. Chem. Ind.*, **36** (1917), 950.

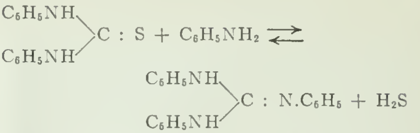
It is not our purpose, however, to attribute the action of certain substances as accelerators entirely to the inclusion and position of certain groups in the primary nucleus. Rather, as has been said, we have been led to the conclusion that the great majority of organic accelerators owe their activity to their decomposition products, when this decomposition takes place in the presence of sulfur and under vulcanizing conditions. This corresponds very closely with Spence's third class of accelerators, which he believes may be inactive in themselves, but which, at the temperature of vulcanization, either alone or in the presence of other substances, may break down into a substance, or substances, having the properties of powerful catalysts. He has mentioned diphenylthiourea as an example of this type.

In the final experiment recorded in this paper, we have worked along these lines with aniline as a standard and have compared its activity with that of other substances into which it can be converted, or from which it can be derived by decomposition under vulcanizing conditions. The following reaction suffices to explain our method:



$$C_6H_5NH_2 + C_6H_6NC:S \rightleftarrows \begin{matrix} C_6H_5NH \\ C_6H_5NH \end{matrix}\!\!>C:S \quad (1)$$

That such a reaction, from right to left, actually takes place was indicated when we found that a mixture vulcanized with the assistance of a certain definite amount of diphenylthiourea had the same sulfur coefficient as that of a similar mixture, vulcanized under the same conditions, to which had been added aniline and phenyl mustard oil, in accordance with the amounts required by Equation 1. Similar sulfur coefficients also resulted for two mixtures, one of which was vulcanized with the assistance of triphenylguanidine and the other with quantities of diphenylthiourea and aniline, in accordance with Equation 2.



$$\begin{matrix} C_6H_5NH \\ C_6H_5NH \end{matrix}\!\!>C:S + C_6H_5NH_2 \rightleftarrows \begin{matrix} C_6H_5NH \\ C_6H_5NH \end{matrix}\!\!>C:N.C_6H_5 + H_2S \quad (2)$$

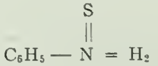
The above reaction, likewise, takes place from right to left. The diphenylthiourea and aniline formed, however, evidently undergo further decomposition with the formation of two molecules of aniline and one molecule of phenyl mustard oil

Our interpretation of these results led us to the conclusion that both diphenylthiourea and triphenylguanidine owe their powers of acceleration to their tendency to decompose with the formation of aniline. On the other hand, and in view of our results as a whole and particularly those obtained with urea and thiourea, we certainly do not feel warranted in ascribing to aniline alone those properties which Spence has termed the "active principle." Rather, we are inclined to regard aniline as one of the simpler substances that contains a group which, under vulcanizing conditions and temperatures, functions as a sulfur carrier.

To elaborate upon the action of accelerators beyond this point, however, is hardly warranted from the results obtained. Moreover, further discussion must, necessarily, involve the theory of vulcanization in its entirety, which is not our intention in this communication.

We have shown that under vulcanizing conditions and temperatures, certain accelerators decompose or suffer degradation to simpler substances which are responsible for the acceleration effected. The decomposition of diphenylthiourea to aniline is an example. Such being the case, similar decompositions would appear possible with other substances. This decomposition having been effected, the action of the decomposition or alteration products is most conveniently interpreted on the basis of a change in the valency of the nitrogen in active groups from 3 to 5.

It is not to be understood, however, that we believe aniline as such is, necessarily and quantitatively, formed by the decomposition of diphenylthiourea under vulcanizing conditions. Further, the various complexes which we have postulated for aniline, *p*-phenylenediamine, etc., serve to account only for the relationship noted between the activity of the substance in question and its nitrogen content. Theoretical deductions of a general nature are not at present possible, as results obtained by Erdmann[1] and Ostromyslenskii[2] indicate that the active sulfur may take the form of a polysulfide and may even not be attached to nitrogen. However, for the purpose of interpretation, rather than deduction, and with aniline as an example, under the conditions and temperatures at which vulcanization takes place, we postulate the existence of the following complex:



$$C_6H_5-\overset{\overset{\displaystyle S}{\|}}{N}=H_2$$

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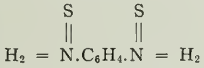
[1] *Ann.*, **362** (1908), 133.

[2] A. H. King, *Met. & Chem. Eng.*, **18** (1918), 245.

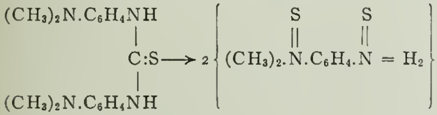
As this complex would not be stable, except under the conditions and temperatures at which vulcanization is effected, it would function as a catalytic sulfur carrier, releasing its sulfur in an active form, which would combine with the rubber more readily than the sulfur originally included in the mixture. Its catalytic action would depend upon its ability to maintain an equilibrium between the active and inactive sulfur.

The above is in strict accord with our results for the relative activity of aniline and *p*-phenylenediamine. The hypothetical complex for the latter substance would include 2 pentavalent nitrogen atoms, or active groups, as below:



$$H_2 = \overset{S}{\overset{\|}{N}}.C_6H_4.\overset{S}{\overset{\|}{N}} = H_2$$

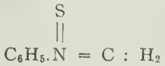
Thus, when the effect of molecularly equivalent quantities of aniline and *p*-phenylenediamine are compared, the latter should be just twice as active as the former. This was actually found to be the case. From this it is also possible to explain why Spence found tetramethyldiaminodiphenylthiourea so much more active than diphenylthiourea; the former substance would probably decompose into 2 molecules of dimethyl-*p*-phenylenediamine with just twice the number of active groups found in the latter. Further, we venture to predict that the activity of one molecular part of tetramethyldiaminodiphenylthiourea is exactly equal to that of 2 equimolecular parts of dimethyl-*p*-phenylenediamine,[1] and less than that of 2 equimolecular parts of *p*-phenylenediamine. The difference in the basicities of the last two substances accounts for their relative activities



$$\begin{array}{l}(CH_3)_2N.C_6H_4NH\\ \qquad\quad |\\ \qquad\quad C{:}S \longrightarrow 2\left\{\begin{array}{c}(CH_3)_2.N.C_6H_4.\overset{S}{\overset{\|}{N}} = H_2\end{array}\right\}\quad (3)\\ \qquad\quad |\\ (CH_3)_2N.C_6H_4NH\end{array}$$

The latter observation is made in the light of our results with the ureas and guanidines. While our results with these substances are subject to the same general interpretation as the preceding, we found with them that the replacement of the hydrogen by phenyl in the active groups decreased the activity of the substance in question. It is possible that the substitution of larger groups for the hydrogen attached to the active nitrogen would cause the group to become inactive, due to steric hindrance precluding the formation of pentavalent nitrogen. Peachey's observation of the inactivity of the nitrosamine isomeric with *p*-nitrosodimethylaniline may be subject to this interpretation.

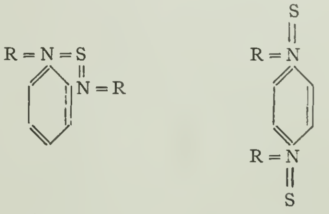
In view of this, our results with the anhydroformaldehyde condensation products of aromatic amines are more difficult to interpret, as the substitution of methylene for hydrogen increased the activity. In this instance, however, there will be two double bonds when nitrogen becomes pentavalent:



$$C_6H_5.\overset{S}{\overset{\|}{N}} = C : H_2$$

A complex of this type would be even more unstable, and more active, than that postulated for aniline.[1]

Lastly, in light of the readiness with which sulfur passes from the di- to the tetra- or hexavalent state, it is possible to adapt the former principles to account for the difference in the relative activities of the *o*- and *p*- products of the same substance. The proximity of two groups in the *o*-position might lead to a complex of type *A*, whereas, if the groups were in the *p*-position, the configuration would be that shown in type *B*.



(*A*) (*B*)

In this case, then, the *p*- would be twice as active as the *o*-product, a condition with which we are not as yet familiar.

In the foregoing we have not taken into consideration the effect of the accelerators upon the physical properties of the mixtures investigated, and have confined our remarks to interpretations made on the basis of excess sulfur coefficients of vulcanization only. However, in our experiments with mixtures vulcanized with the assistance of aniline, diphenylthiourea and triphenylguanidine, we were able in no instance to recover the original amount of the accelerator in the acetone extract. While this does not permit us to state definitely that a portion of the accelerator or its decomposition products, as well as the sulfur, becomes closely bound to the rubber molecule, it is not impossible that such is the case. We agree with King, that the remarkable improvement imparted to mixtures vulcanized with the assistance of certain organic accelerators indicates that the binding between the

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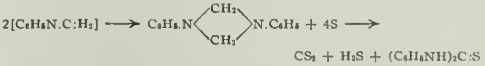
[1] It is interesting to note that Eaton, Grantham and Day (Dept. of Agr. Fed. Malay States, *Bulletin* **27** (1918), 319) found dimethyl-*p*-phenylenediamine hydrochloride to exert a marked retarding influence upon the vulcanization of a fast curing rubber. In this case, then, the nitrogen of the amino group is already pentavalent, and could not act as a sulfur carrier; it has already been shown that acid groups act as retardants.

In this connection, it should also be pointed out that although dimethyl-*p*-phenylenediamine is more active than aniline, dimethylaniline is practically inert.

[1] In the paper by C. W. Bedford and W. Scott, read immediately after the above, the following explanation was offered for the behavior of this substance. According to the above authors, under vulcanizing conditions and temperatures, the following reactions take place:



$$2[C_6H_5N.C{:}H_2] \longrightarrow C_6H_5.N\begin{smallmatrix}CH_2\\ CH_2\end{smallmatrix}N.C_6H_5 + 4S \longrightarrow CS_2 + H_2S + (C_6H_5NH)_2C{:}S$$

We have already shown that diphenylthiourea probably decomposes into aniline and phenyl mustard oil. Further, we have shown that when compared on equal weights the activities of anhydro-formaldehyde aniline and diphenylthiourea are approximately the same. As the molecular weight of diphenylthiourea is over twice that of anhydro-formaldehyde aniline, and as two molecules of the latter and one molecule of the former would each decompose into one molecule of aniline, a comparison with equal weight of the two substances should show anhydro-formaldehyde aniline to be slightly more active than diphenylthiourea. This is in strict accordance with the above reactions and our findings.

"active principle," or active group, of certain of the organic accelerators and the rubber is a close one.

In the course of another investigation shortly to be published, we have shown that fundamental differences exist between vulcanized mixtures of rubber and sulfur, and similar mixtures vulcanized with the assistance of an organic accelerator. This is subject to still further modification if either type of mixture contains a mineral oxide.

EXPERIMENTAL PART

The same general method of procedure was pursued in this work as in that previously reported.

The rubber used was good quality, first latex, pale crêpe, and the same lot was employed in all mixtures. All mixtures were made under standard conditions; the average time of each batch on the mill was 17.5 min. The same proportion of rubber and sulfur—92.5 parts rubber, and 7.5 parts sulfur—was employed in each instance, but the amount of accelerator was varied, according to the conditions of the experiment.

All of the accelerators soluble in alcohol were dissolved in the smallest quantity of this liquid and introduced into the rubber in solution. Those not soluble—and this applied to the anhydro-formaldehyde bodies only—were ground to 100 mesh and added to the rubber with the sulfur. After mixing, the mixtures were allowed a recovery period of 24 hrs. before they were vulcanized. Vulcanization was carried on in a platen press of the usual type.

The vulcanized sample for analysis was then sheeted thin on the mill, subjected to 24 hrs. continuous extraction with acetone in the extractor recommended by the Joint Rubber Insulation Committee,[1] dried in air and *in vacuo* at 100° C. to constant weight. The free, or extractable, sulfur found in the acetone extract was estimated by the bromine oxidation method of the Bureau of Standards.[2] The combined sulfur in the extracted rubber was estimated by a method of our own, to be reported upon in the near future.[3] All figures given for per cent sulfur are the average of at least 2 determinations which checked to within 0.1 per cent.

PRELIMINARY EXPERIMENTS—With the exception of aniline, which was purified by distillation and boiled at 185° C., all of the accelerators shown in Table I were recrystallized from alcohol. The purified products were found to have the following melting points: urea, 132° C.; thiourea, 168° C.; monophenylthiourea, 153° C.; diphenylthiourea, 151° C.; monophenylguanidine, 193° C.; *sym*-diphenylguanidine, 147° C.; triphenylguanidine, 143° C.

In the case of the substances shown in Table II, the *p*-phenylenediamine was recrystallized from alcohol and melted at 146° C. The anhydro-formaldehyde bodies possessed the following melting points: anhydro-formaldehyde aniline, 140° C. (with decomposition); monoanhydro-formaldehyde *p*-phenylenediamine, 142° C.: dianhydro-formaldehyde *p*-phenylenediamine, 192° C.

TABLE I—RELATIVE ACTIVITIES—THIOUREA SERIES

Parts Required to Equal One Part Aniline

Aniline	1.000
Urea	0.250
Thiourea	0.300
Monophenylthiourea	0.450
Diphenylthiourea	0.850
Monophenylguanidine (α)	0.075
Diphenylguanidine (*Sym*)	0.075
Triphenylguanidine	0.500

The activities of the various substances were compared in the mixture previously mentioned—92.5 parts of rubber and 7.5 parts of sulfur—taking as a standard[1] the effect obtained with one part of aniline, vulcanized for 90 min. at 148° C. The amounts of various substances in the urea series required to effect the same degree of vulcanization as obtained with one part of aniline are shown in Table I. The same is true for the anhydro-formaldehyde aniline series, the results of which are shown in Table II.

TABLE II—RELATIVE ACTIVITIES—ANHYDRO-FORMALDEHYDE SERIES

Parts Required to Equal One Part Aniline

Aniline	1.00
Anhydro-formaldehyde aniline	0.75
p-Phenylenediamine	0.17
Monoanhydro-formaldehyde *p*-phenylenediamine	0.14
Dianhydro-formaldehyde *p*-phenylenediamine	0.14

As these preliminary tests were conducted solely to obtain information for guidance in subsequent experiments, and as no sulfur estimations were made, we do not feel warranted in drawing extensive conclusions from them. It would appear, however, that in the case of the urea series, the introduction of phenyl as a substituent for the hydrogen of the amido or imido group is responsible for a marked decrease in the activity of the parent substance. Also, in the case of the anhydro-formaldehyde series, it is evident that the introduction of the second amino group into the benzene nucleus increases the activity of the substance to a greater extent than substituting methylene for the hydrogen in the original amino group.

FINAL EXPERIMENTS—(I) This experiment was carried out in order to determine the relative accelerating effects produced by certain substances which contained hydroxyl or amino groups in their primary nucleus. Determinations were also made of the effect produced when the number, or kinds, of groups in the nucleus were altered or changed.

Every effort was made to obtain the various substances in the greatest degree of purity. Their physical constants were as follows: phenol, m. p. 41° C.; *p*-amidophenol, sublimed at about 180° C.; aniline, b. p. 185° C.; hydroquinone, m. p. 168° C.; *p*-phenylenediamine, m. p. 146° C.

The relative activity of these substances, as expressed by their sulfur coefficients, is shown in Table III.

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[1] This Journal, **6** (1914), 514.

[2] Bureau of Standards, *Circular* **38** (1915), 66.

[3] This method was evolved and applied in the course of the present work, in order to overcome certain disadvantages in the Rosenstein-Davies method (*Chemist-Analyst*, **15** (1915), 4) previously employed.

[1] The comparisons were made at what was judged to be in each case the correct cure, as measured by the physical properties of the various mixtures only. Owing to this fact, the values assigned in Tables I and II were not found to be in strict agreement with their respective sulfur coefficients as determined in the subsequent experiments. Such comparisons, based on physical properties alone, are apt to be misleading, due to the toughening action imparted to the rubber when certain accelerators are employed; this effect is very noticeable in the case of *p*-phenylenediamine.

TABLE III—RELATIVE ACCELERATION

First Latex Pale Crêpe.................. 92.5 parts
Sulfur.................................. 7.5 parts
Accelerator............................. 1 part
Vulcanized for 90 min. at 148° C.

ADDED SUBSTANCE	Combined Sulfur Per cent	Sulfur Coefficient	Excess Sulfur Coefficient	Group Coefficient
Control	1.792	1.937	...	...
Phenol	1.629	1.779	—0.158	—0.00168
Hydroquinone	1.430	1.561	—0.376	—0.00170
p-Amidophenol	4.772	5.210	+3.273	...
Aniline	4.226	4.614	+2.677	+0.02870
p-Phenylenediamine[1]	7.286	7.955	+6.018	+0.02780

[1] As the combined sulfur obtained in this instance is so close to the total amount originally added to the mixture, this comparison was repeated with 0.25 per cent aniline and *p*-phenylenediamine. When employed in this amount, aniline gave an excess sulfur coefficient of 1.421 and *p*-phenylenediamine, 3.552. On calculation, their group coefficients were found to be 0.01530 and 0.01640, respectively.

From this table, it is seen that phenol, when expressed in terms of its sulfur coefficient, has a slight retarding influence which is almost exactly doubled in the case of hydroquinone, when the molecular weight of the latter is taken into consideration. Aniline and *p*-phenylenediamine are seen to exert a marked accelerating effect, as would be expected, and here, again, the effect produced by two amino groups is almost exactly twice that of a single group when the molecular weights of the two substances (aniline and *p*-phenylenediamine) are taken into consideration.[1] Thus, when equal weights of certain accelerators which contain active groups in the same primary nucleus are employed, it is possible to compare the activity of these groups *per se* by means of a group coefficient. Or, conversely, molecular quantities of substances which contain the same active group (or groups, if in equal number) in the primary nucleus should produce the same accelerating activity.

In the case of equal quantities by weight, this may be expressed as follows:

$$\text{Group coefficient} = \frac{Sx}{Mn}$$

where Sx = the excess sulfur coefficient over that of a control mixture vulcanized without an accelerator.
M = the molecular weight of the accelerator.
n = the number of the groups in the primary nucleus.[2]

When the results recorded in Table III are substituted in the above expression, the coefficient for the (OH) group is seen to be in good agreement for both phenol and hydroquinone; the same is true for the coefficients obtained for the (NH_2) group in both aniline and *p*-phenylenediamine. In other words, the introduction of a second group in the para position just doubles the activity. In light of our remarks in the introductory part of this paper, in regard to the function of these groups in accelerating the reaction between rubber and sulfur, we regard this point of much more importance than the numerical coefficient of the group itself, although a properly arranged table of group coefficients would undoubtedly be of value in anticipating the activities of untried substances.

II—In the previous experiment we employed substances of comparatively simple composition, and have attributed their action as accelerators to the presence of certain active groups. In the introductory part of this paper, however, we have pointed out that the action of certain other accelerators depends upon their ability to decompose, under vulcanizing conditions and temperatures, into degradation products containing an active group which is responsible for the acceleration effected. The present experiment was designed to further emphasize this point.

For this purpose, diphenylthiourea was chosen as the standard accelerator, on the assumption that Equation 1 is reversible and proceeds from right to left under the conditions and temperatures at which vulcanization ordinarily takes place.

Such being the case, and in view of the probable inactivity of phenyl mustard oil, the activity exerted by one part of diphenylthiourea should be no greater than that effected by a quantity of aniline corresponding to the amount required for the above reaction, when it is proceeding towards the left. Likewise, if the accelerating effect obtained with diphenylthiourea is dependent solely upon the amount of aniline formed by the decomposition of the former substance during vulcanization, the same should be true for triphenylguanidine, in accordance with Equation 2, which should also proceed from right to left during the vulcanization.

As mentioned in the introductory part of this paper, the diphenylthiourea and aniline formed undoubtedly undergo a subsequent decomposition with the formation of 2 molecules of aniline, and 1 molecule of phenyl mustard oil.

In order to test the above, our standard mixture was vulcanized for 90 min. at 148° C., with the assistance of one part of diphenylthiourea, and compared with similar mixtures which contained molecularly equivalent amounts of either one or both of the various decomposition products indicated in the above equations. The actual amounts of the different substances employed are shown in the second column of Table IV; they showed the following physical constants: phenyl mustard oil, b. p. 220° C.; aniline, 185° C.; diphenylthiourea, m. p. 151° C.; triphenylguanidine, m. p., 143° C.

Before any sulfur determinations were made, the different slabs were submitted to thumb and tooth tests in order that a rough estimation of their relative physical properties might be recorded. As shown in Table IV, the control has been used as the standard for comparison and given the number 1. The value 2, given to diphenylthiourea, simply indicates that it was faster than 1; number 3 was considered faster than 2, and so on for the rest of the series. The differences existing between the physical properties of the various slabs, however, were in no sense proportional to the numbers given them. The odor of the cured slabs was recorded in each instance and found to substantiate

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[1] The alkaloidal substances mentioned by Spence as decidedly active are undoubtedly of a high molecular weight.

[2] The term "nucleus" is used as distinct from "molecule," in order to preclude the inclusion of similar groups in the side chains which, as Peachey has already noted, are not comparable in the effect produced. Likewise, as our work has been confined to two groups in the para position, further extension of this principle would require the introduction of another factor to compensate for the appearance of groups in the meta and ortho positions. In the most cases, the ortho, meta and para products are increasingly active in the order named. Such differentiations, however, may be carried on indefinitely to include naphthylamines, etc. We have found β-naphthylamine to be almost twice as active as α-naphthylamine.

TABLE IV

First Latex Pale Crêpe....... 92.5 parts
Sulfur..................... 7.5 parts
Accelerator.................... X parts
Vulcanized for 90 min. at 148° C.

	X = Parts Accelerator Added to the Mixture	Physical Properties	ODOR OF CURED SLAB	—Acetone Extract— Per cent (Uncorrected)	Per cent (Corrected)	Free Sulfur Per cent	Combined Sulfur Per cent	Total Sulfur Per cent (By Addition)
Control....	0.00	1	Standard	8.630	2.894	5.736	1.792	7.528
Phenyl Mustard Oil...........	0.59	—1	Phenyl mustard oil	8.443	2.729	5.714	1.726	7.440
Aniline......................	0.41	4	Decomposition products of aniline	7.065	3.137	3.928	3.625	7.553
Phenyl Mustard Oil and Aniline	C_6H_5NCS = 0.59 $C_6H_5NH_2$ = 0.41	3	Phenyl mustard oil and decomposition products of aniline, the latter predominating	7.966	3.595	4.371	3.100	7.471
Diphenylthiourea	1.0	2	Phenyl mustard oil and decomposition products of aniline, the latter predominating	7.429	3.119	4.310	3.078	7.388
Diphenylthiourea and Aniline....	$(C_6H_5NH)_2CS$ = 1.0 $C_6H_5NH_2$ = 0.41	6	Decomposition products of aniline predominating	7.301	3.963	3.338	3.959	7.297
Triphenylguanidine............	1.25	5	Strong, but indistinguishable. Phenyl mustard oil could be detected	7.523	4.063	3.460	3.872	7.332

the preceding equations. The results obtained for the acetone extracts of the different mixtures, together with all the sulfur estimations made, are also recorded in detail in Table IV. To facilitate comparison, the combined sulfurs, expressed as sulfur coefficients, are tabulated in Table V in the order of their relative magnitude.

TABLE V

First Latex Pale Crêpe......... 92.5 parts
Sulfur........................ 7.5 parts
Accelerator.................... X parts
Vulcanized for 90 min. at 148° C.

ACCELERATOR	Combined Sulfur Per cent	Sulfur Coefficient	Excess (+) Sulfur Coefficient
Phenyl Mustard Oil..................	1.726	1.877	—0.060
Control (No Accelerator)..............	1.792	1.937	...
Diphenylthiourea.....................	3.078	3.361	1.424
Phenyl Mustard Oil and Aniline.........	3.100	3.385	1.448
Aniline..............................	3.625	3.935	1.998
Triphenylguanidine....................	3.872	4.240	2.303
Diphenylthiourea and Aniline...........	3.959	4.340	2.403

From Table V it is seen that the sulfur coefficients obtained confirmed very closely the estimates made upon the physical properties. Further, it is shown that the activity of diphenylthiourea is almost exactly equal to that obtained with an amount of aniline corresponding to the quantity formed in its decomposition products as expressed in Equation 1. Likewise, triphenylguanidine was found to have the same activity as obtained with an equivalent amount of diphenylthiourea and aniline, as required by Equation 2, when the reaction proceeds toward the left.

It is evident that the action of both diphenylthiourea and triphenylguanidine as accelerators is due to their tendency to decompose, under vulcanizing conditions and temperatures, with aniline as one of the most probable degradation products. Moreover, it would appear that the aniline so formed is responsible for the acceleration effected, and owes its activity to the presence of an active group containing nitrogen, which functions as a sulfur carrier. That in no case were we able to recover the original amount of accelerator in the acetone extract, is an indication—and an indication only—that a portion of the active principle may also remain bound to the rubber as well as the sulfur.

Final emphasis is laid upon the fact that all of our results have been obtained with a mixture composed of rubber, sulfur, and accelerator only. The presence in the mixture of inorganic oxides has been found to have a marked influence on both the chemical and physical results obtained after vulcanization.

CONCLUSIONS

In view of the preceding results, we have been led to the following conclusions:

1—Comparisons of organic substances as accelerators should be made with molecularly equivalent amounts of the substances in question, and should be based on the values obtained for their excess sulfur coefficients over that of a control which contains no accelerator.

2—The action of certain substances, such as diphenylthiourea, is due to their tendency to decompose under vulcanizing conditions and temperatures into simpler substances which contain an active nitrogen group which is responsible for the acceleration effected.

3—Molecularly equivalent quantities of substances which contain the same active nitrogen group in their primary nucleus effect the same accelerating activity.

4—The replacement of the hydrogen in the active nitrogen group by other and larger groups, or radicals, decreases the activity of the parent substance.

5—The activity of the nitrogen in certain groups is most readily interpreted as due to a change in valency from three to five, with the temporary addition of sulfur; the active nitrogen group would thus function as a sulfur carrier.

CARBON BLACK—ITS PROPERTIES AND USES[1,2]

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An investigation of the carbon black industry has been undertaken by the United States Bureau of Mines as a result of economic issues brought up during the war. In the present process of manufacture carbon black is made by burning natural gas with a supply of air insufficient for complete combustion and collecting the liberated carbon on a metal surface by actual contact of the flame on the surface. This process produces from 0.5 lb. to 1.5 lbs. of carbon black from 1000 cu. ft. of gas or 1.5 per cent to 3.5 per cent of the total carbon in the gas. The process at first sight seems most wasteful but examination of the problem shows that it is at any rate the only process in practical operation which produces carbon black

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[1] Published by permission of the Director, U. S. Bureau of Mines.

[2] Presented at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

suitable for the ink trade and rubber industry consumers whose combined use is over 30,000,000 lbs. annually. The whole situation appears to necessitate thorough investigation before any opinion can be given in regard to the wastefulness of the present process.

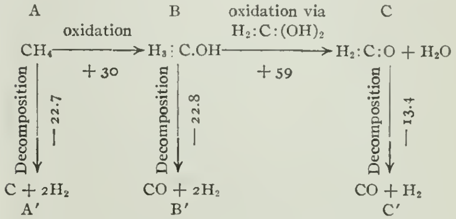
Accordingly the industry has been carefully studied as to methods of manufacture, properties, and uses of the finished product. Plants in Louisiana, Oklahoma, and West Virginia have been studied by Bureau engineers. Other processes for making carbon black have been investigated. The uses of carbon black have been studied with the idea of determining the properties of the product which users of carbon black demand and with an attempt at designating in which of these uses carbon black is essential and in which a substitute material might be employed. Microscopic investigation of a large number of blacks has been made and test methods studied with a view to finding the reason for the very different behavior exhibited by different blacks.

METHOD OF MANUFACTURE

Carbon black, as known to the American trade, is the fluffy, velvety black pigment produced by burning natural gas with a smoky flame against a metal surface. It is entirely different in physical characteristics from lampblack, which is made by burning oil or other carbonaceous material with insufficient air for complete combustion and collecting the smoke in settling chambers. Lampblack is gray in contrast to the deep black of carbon black, often contains considerable quantities of empyreumatic matter, and when used in printing ink gives a product with very different properties from an ink of similar composition made from carbon black. The process of manufacture used to the greatest extent at the present time is the so-called channel system, in which the black is deposited on the smooth under-surface of steel channels by lava-tip burners set at a distance of 3 or 4 in. below the channel. The channel irons are usually built up in tables of eight, sometimes 100 ft. long, and are given a slow reciprocating motion which scrapes the black deposited on them into hoppers from which it is carried by screw conveyors to the packing house, where it is bolted and sacked. The mechanism is enclosed in sheet-iron buildings in order that the amount of air may be regulated. Varying the amount of air, speed of scraping, and pressure of the gas controls the quality of the product. The shape of the burner and distance from the collecting surface also affects the quality of the black, but these are constant for any one plant. Other similar processes differ only in the nature of the collecting surface and burners. Godfrey L. Cabot, a pioneer in the carbon black industry, has described in a very able manner the history of the development of the manufacture of carbon black.[1] Mr. R. O. Neal, of the Bartlesville Station of the Bureau of Mines, is preparing a technical paper describing in detail the present method of manufacture and discussing the economic side of the industry.

THEORY OF FORMATION OF CARBON BLACK

When natural gas burns in an incomplete supply of air, the carbon is liberated, not as a result of preferential combustion of hydrogen, but as a direct decomposition of unburned gas in the heat of the flame. According to Bone[1] and co-workers, combustion takes place in steps as a result of hydroxylation:



It is evident that the tendency is always to run from A to C. When the proportion of methane to oxygen is $CH_4 : O_2$ the reaction goes from A to B to C to C′. If the ratio is $2\ CH_4 : O_2$ or higher, only a part of the methane can be oxidized through the reaction A to C and part is decomposed at A by the heat evolved in the A to C reaction. The lowest per cent of oxygen in which a methane flame will burn is 15.6 per cent. Carbon will be evolved only in the inner part of the flame, where the oxygen supply is low but where there is sufficient heat to break up the methane, and the per cent of carbon to be expected by the incomplete combustion of methane is low. Gases rich in ethane and the higher homologs produce greater yields by this process.

The function of the cold surface is to cool the liberated carbon in the flame sufficiently to prevent its combustion. This permits the use of a sufficiently hot flame to give carbon uncontaminated with hydrocarbons or their partial oxidation products and produces a finely divided material which has been prevented from agglomerating by the sudden cooling. It is evident that there must be an optimum temperature and an optimum position for the surface in the flame. Too cold a surface may prevent the maximum separation of carbon; too hot a surface will allow too much carbon to be burned and may change the properties of the carbon which remains unburned. The temperature of the channels in the present processes is about 300° C.

Numerous methods for producing a larger yield of carbon black from natural gas have been proposed and patented. In most of these processes the gas is broken up into carbon and hydrogen by passing through a retort filled with refractory material at a temperature of 1200° C. or over. A much higher yield of carbon, sometimes as high as 40 per cent of the theoretical, is produced in this way, but it has not yet been made of a grade commercially salable. The carbon, while often finely divided, is usually gray in color and contains particles of grit which may be agglomerates of carbon or particles of the refractory material. It seems highly possible, however, that with properly controlled conditions a carbon suitable for use in rubber might be made by this method. The hydrogen produced can be sold at a nice profit and even if the hydrogen were not used, the black could be produced for less than 5 cts. a lb. For use in ink, carbon black made by the closed retort method up to the present time has been of no value, due to inferior color, grittiness, and low oil absorption. The defect with methods thus far developed has been that the carbon after being liberated stayed in the heated zone long enough to become partially agglomerated and changed into the gray modification of amorphous carbon. Experimental work along this line should aim to crack the carbon on a thin layer of catalyst at as low a temperature as possible and to get it away from the heated zone immediately after formation, or to catch it on a cold surface near the catalyst.

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[1] *8th Intern. Cong. Applied Chem.*, **12**, 13.,

[1] *Trans. Roy. Soc. London*, **215** (1915), 275.

Other methods have been patented, *e. g.*, chlorination of natural gas to hydrochloric acid and carbon black, explosion of acetylene, rupture of hydrocarbon vapors with electric spark, exploding hydrocarbon vapors with CO, CO_2 and O_2, but to the authors' knowledge none of them have ever produced any quantity of a salable product in this country.

USES OF CARBON BLACK

In order of importance the uses of carbon black are as follows:

1—Printers' ink.

2—Automobile tires and other rubber goods.

3—Black and gray paint and enamel.

4—Stove polish.

5—Other products—such as phonograph records, carbon paper, crayons, typewriter ribbons, black and gray paper, glazed paper, tarpaulins, black leather, bookbinders' board, marking and stenciling inks, rubber sheeting and clothing, hard rubber, artificial stone and black tile, Chinese and India inks, fireworks, insulating materials, crucible steel, case hardening.

The amounts used by these industries in 1918 were approximately as follows:

	Pounds
Printers' ink	10,000,000–12,000,000
Rubber goods	20,000,000
Stove polish	4,000,000–5,000,000
All others	1,000,000

Besides this, in normal times probably 15,000,000 lbs. are exported.

PRINTERS' INK—Lampblack has been used as a pigment for printers' ink ever since the invention of the printing press, and was used almost exclusively up to 1864. For certain sorts of printing where an extremely fine-grained ink was required, great trouble was taken to purify the black, but after the advent of carbon black in 1864, and its increased production and diminished cost after 1880, lampblack became less and less used in the ink trade, and at the present time only a small amount is used, and then only to impart certain qualities to an ink already containing carbon black.

Carbon black has certain properties which make it peculiarly suitable to the needs of the modern printing art. It is well adapted to the modern fast running presses and to the fine half-tone screen work which enters into most of our illustrations. Certain carbon blacks give what is known as a short ink, that is, an ink of buttery consistency which does not flow rapidly. This is especially desirable in lithographic and offset work, and in slow speed presses and most half-tone work. Lampblack does not give the right consistency for such work and is too gray in color. For fast running presses, carbon black made by other processes is also good in that it makes a very fluid long ink which at the same time has sufficient opacity to give a black letter obscuring the paper well. Ink manufacturers and users believe that carbon black is absolutely essential to their business.

RUBBER TIRES—Prior to 1914 little carbon black was used by the rubber industry and then only in small amounts as a coloring material. Little distinction was made between carbon black and lampblack, the two compounds being used indiscriminately. At this time, due partly to the stimulus afforded by the rising price of zinc oxide, it was found that carbon black could be used in very large amounts as a filler for rubber, with a correspondingly smaller amount of zinc oxide. Carbon black is used in rubber in quantities of 3 per cent to 20 per cent by weight. Many manufacturers claim very unusual properties for rubber so compounded. It is said to increase the tensile strength very greatly and to give increased toughness and resistance to abrasion. It is believed by some authorities that the life of the rubber is increased. Other rubber chemists are more conservative in their praises of carbon black and do not admit that it possesses any properties which make it irreplaceable.

From the point of view of cost, carbon black is much cheaper than zinc oxide. Carbon black, absolute specific gravity 1.8, suitable for compounding in rubber, can be procured as low as 10 cts. a lb. at the present time. Zinc oxide costs at least as much and has a specific gravity of 5.8. Carbon black evidently costs one-third as much as zinc oxide on a volume basis, supposing that equal volumes were compounded with the rubber, but in practice a greater volume of carbon black is used than of zinc oxide so that the resulting mix with carbon black contains less rubber per unit volume than the corresponding zinc oxide mix.

From a theoretical consideration, carbon black should be an ideal filler for rubber on account of its extremely fine state of division and the correspondingly large surface energy developed when intimately mixed with the gum rubber. It also serves to protect the rubber substance from the effects of light and may possibly retard oxidation.

Whatever may be the true state of affairs as to the irreplaceability of carbon black in rubber, an enormous amount is now consumed by the rubber companies, probably 20,000,000 lbs. annually, and 10,000,000 lbs. exported for foreign trade in normal times.

PAINT—Carbon black is coming into extensive use in the paint trade. It has a higher tinting strength than any other black and a given weight will obscure a greater area of surface. Carbon black is acknowledged superior in varnishes and enamels and evidently has many followers in making black and gray paints for general purposes. The U. S. War Department requires the use of carbon black in black enamels and various black and gray paints for general purposes. Some authorities consider lampblack superior to carbon black and it is probably true that in certain gray tints lampblack is superior, owing to its bluish gray tones.

OTHER USES—For other purposes carbon black is employed chiefly because of its cheapness and high coloring power. It produces a carbon paper of very smooth surface which will give a large number of copies before the letters lose their opacity. For phonograph records it gives a smooth surface for recording the vibrations, although lampblack is often used for this latter purpose.

TESTING METHODS

The final test of the suitability of a black for a given purpose is the actual trying out of the working qualities. In rubber making a sample mix is made and the finished piece tested for tensile strength, per cent elongation, toughness, and resistance to abrasion. In ink making a sample batch of ink is made up and the suitability of the black determined by an actual run on the press for which the ink is intended, in which the working qualities of the ink and the amount used for a given number of impressions are noted.[1]

There are, however, a number of laboratory tests which are of use in matching a standard sample. The tests most commonly employed are for tinting strength, color, and grit. It is also desirable to determine moisture, ash, and acetone extract.

TINTING STRENGTH—According to the American Society for Testing Materials, tinting strength is "the power of coloring a given quantity of paint or pigment selected as a medium or standard for estimating such power." Tinting strength, then, as applied to carbon blacks is the measure of the ability of the black to impart a color to a definite weight of standard white. It depends on the size of the particles and the specific gravity of the black. In making the test, the black is always compared with a standard black.

Weigh out accurately on a sensitive balance, 0.100 g. of the black to be tested and 10.0 g. of a standard zinc white kept especially for the purpose. Transfer to a glass or marble slab and add from a burette exactly 3.5 cc. refined linseed oil. Mix with a palette knife and rub out thoroughly with the palette knife (or, better, a glass muller) until no streakiness or difference of color is observed, when successive small portions are spread out on a clean piece of window glass and viewed from the upper side. It is important that the rubbing out be thorough; 10 min. are usually sufficient. Follow the same procedure with the standard black. Then spread a small amount of each mix side by side on a clean glass (a microscope object glass serves the purpose very nicely). Examination of the samples from the other side of the glass, particularly at the line where they overlap, will show the difference in tinting strength.

To make a quantitative estimation of the tinting strength of the sample as compared to the standard, more white is added to the stronger mix until the colors match. A new sample of the stronger black is then weighed out, using the calculated amount of zinc white, and the process repeated until mixes of the same color are obtained. If, for example, it was necessary to mix 15 g. of zinc white with 0.1 g. of the standard to match a mixture of 10 g. zinc white and 0.1 g. of the sample, the latter has two-thirds the strength of the standard.

COLOR—By this term is meant the relative blackness of the material when mixed in oil.

To 0.3 g. of each of the blacks to be compared add 1.3 cc. of refined linseed oil from a burette. Mix thoroughly with the palette knife and spread side by side on a slip of glass and compare the relative color by viewing from the upper side of the glass.

GRIT—Presence of gritty matter is determined by rubbing a portion of the black under the finger or by placing a small amount on the tongue and rubbing between the tongue and palate.

CHEMICAL TESTS—It is occasionally desirable to make a few quantitative chemical tests of carbon black. A black containing more than 0.2 per cent ash is probably adulterated with mineral black or charcoal. An acetone extract over 0.1 per cent indicates adulteration with a poorly calcined lampblack. Too great a percentage of moisture is undesirable from the point of view of working qualities. Certain blacks will absorb as much as 15 per cent of their weight of moisture, making a total moisture content of 20 per cent or more. Most blacks for ink making contain from 2 to 4 per cent of moisture, although certain blacks may contain as high as 7 per cent.

Moisture[1]—A 1-g. sample of the black is placed in a weighed porcelain crucible and heated for one hour at 105° C. in a constant temperature oven in circulating dry air. The crucible is then removed from the oven, covered, and cooled in a desiccator over sulfuric acid. The loss in weight multiplied by 100 is recorded as the percentage of moisture.

Ash[1]—The crucible containing the residue from the moisture determination is heated gradually with a Meker burner (or better, in a muffle furnace) to cherry-red (about 750° C.). Ignition is continued until all the particles of carbon have disappeared. The crucible is then cooled in a desiccator and weighed, after which it is heated again for 15 min., cooled in a desiccator, and reweighed. If the change in weight is more than 0.0002 g., the process is repeated until successive weighings are constant to this figure. The weight of the crucible and ash minus the weight of the crucible is taken as the weight of the ash.

Acetone Extract—A 2-g. sample is weighed into an alundum or paper extraction thimble of 20 cc. capacity and the extraction carried out for one hour, using any standard apparatus of the Soxhlet type. The weight of the residue after evaporation of the acetone is taken as the acetone extract. The extract for a pure carbon black is usually zero.

SPECIFICATIONS

The Bureau has received a great many inquiries in regard to tests which a carbon black must meet to be suitable for use in printing ink or rubber.

The following specifications represent an attempt to gather together the requirements adopted by the trade. It should be realized that there are no hard and fast specifications for carbon black, and that the test on which a black stands or falls is the practical test.

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[1] For a detailed discussion of printing inks see Norman Underwood and John V. Sullivan, "The Chemistry and Technology of Printing Inks," Van Nostrand Co., 1915; "The Composition, Properties, and Testing of Printing Inks," Bureau of Standards, *Circular* **53**, Government Printing Office, Washington, 1915.

[1] For details of method, see F. M. Stanton and A. C. Fieldner, "Methods for Analyzing Coal and Coke." Bureau of Mines, *Technical Paper* **8**.

I—PRINTING INK

Chemical Tests

Moisture—Less than 5.0 per cent
Ash—Less than 0.1 per cent
Acetone Extract—Less than 0.1 per cent

Physical Tests

Color—Must match standard
Tinting Strength—Must equal standard
Grit—None

Practical Tests

The black when made into ink must have satisfactory working qualities as determined by an actual run on the press for which the ink is intended. The ink must have satisfactory transfer, tack, drying properties, color, and must print a sufficient number of pages per pound The oil must not separate from the pigment and there must be no offset or smutting.

II—RUBBER

Chemical Tests

Moisture—Less than 4 per cent
Acetone Extract—Less than 0.5 per cent
Ash—Less than 0.25 per cent

Physical Tests

Grit—None
Tinting Strength—Not less than 90 per cent of the strength of standard

Practical Tests

Rubber mixes are made up containing equal weight of the sample to be tested and of the standard. Mixes are cured under exactly the same conditions. The finished sheet is tested for tensile strength, per cent elongation, toughness, and resistance to abrasion.

III—PAINT

Chemical Tests

Moisture—Less than 5 per cent
Ash—Less than 1.25 per cent

Physical Tests

Grit—None
Tinting Strength—Not less than 95 per cent of the strength of standard

PRELIMINARY WORK ON OTHER LABORATORY TESTS

Some preliminary work has been done on the problem of devising tests which will predict in a quantitative way the performance of the black when made into ink.

Tests which suggest themselves are measurements of viscosity, cohesion, and adhesion of mixtures of black and oil. Determination of these three properties should throw light on the probable performance of the black in use.

VISCOSITY—Attempts to measure the viscosity of mixtures of black and linseed oil in a Saybolt viscosimeter were unsatisfactory because an extremely dilute mixture was necessary. Accordingly, it was decided to try out the MacMichael torsion viscosimeter[1] which is used in the Petroleum Laboratory at the Pittsburgh Station for determining the viscosity of heavy oils. In this instrument a brass disk connected to a graduated torsion head is suspended from a piano wire in a rotating cup containing the liquid to be tested. Deflection times the time of one revolution is proportional to the viscosity. By use of suitable wire, liquids of very high viscosity can be tested. The apparatus is calibrated with a liquid of known viscosity.

Mixtures of equal weights of various blacks with the same amount of raw linseed oil were made up and the viscosity determined by means of the MacMichael apparatus. It was found that carbon blacks prized by ink makers on account of their "length" gave a lower reading on the viscosimeter than other blacks.

At this time the author's attention was drawn to an illuminating paper by Bingham and Green[1] on measurements of the mobility and "yield value" of paint. Bingham distinguishes between the *viscosity* of true liquids and the *rigidity* of plastic solids. Measurements of the flow through a capillary when different pressures are applied to the liquid show that the curve of pressure against the volume flowing through in unit time is different for true liquids and for plastic solids. In a true liquid the curve passes through the origin; for a plastic solid the curve cuts the pressure axis at some distance on one side of the origin. This distance Bingham calls the yield value or force which must be applied to the plastic solid before any deformation takes place.

It appeared possible to obtain similar curves using the torsion viscosimeter by measuring the deflection at different speeds of rotation, the speed of rotation corresponding to the volume flowing through the capillary and the deflection corresponding to the pressure.

Mixes of several blacks were made up, using 10 g. of black to 100 cc. of raw linseed oil. They were run at different speeds in the torsion viscosimeter at a temperature of 80° F. Curves are shown in Fig. 1.

It will be noticed that at the higher speeds the points lie on a straight line and that the extrapolation of this line back to zero r. p. m. does not pass through zero deflection. These curves are similar to those obtained by Bingham with the capillary method. It is possible to obtain a relative figure for the rigidity or mobility and the yield value from these data from the formula

$$R_{\text{rel.}} = t(d_t - d_{t_\infty})$$

where t is the time of one revolution in seconds, d_t the deflection, and $d^t{}_\infty$ the deflection at zero r. p. m.

Data and calculated relative rigidity and mobility are given in Table I.

TABLE I—VISCOSITY OF MIXTURES OF CARBON BLACK AND LAMPBLACK WITH LINSEED OIL

Rev. per Min.	Deflection	Time of One Revolution Seconds	Relative Rigidity	Relative Mobility
		SHORT CARBON BLACK		
124	90	0.48	15.4	0.0650
80	79	0.75	15.7	0.0637
47	70	1.28	15.4	0.0650
21	59	2.86	..	....
11	54	5.45	..	....
Yield Value =	58			
		LAMPBLACK		
124	78	0.48	20.6	0.0486
90	66	0.67	20.8	0.0481
63	57	0.95	20.9	0.0478
38	46	1.58	17.4	0.0575
Yield Value =	35			
		LONG CARBON BLACK		
124	55	0.48	15.4	0.0650
102	49	0.59	15.3	0.0654
67	40	0.90	15.2	0.0658
33	31	1.82	14.6	0.0685
11	22	5.45	..	....
Yield Value =	23			
		RAW LINSEED OIL		
124	7	0.48	3.4	0.0194
70	4	0.86	3.4	0.0194
Yield Value =	0			

SUMMARY

	Relative Rigidity	Relative Mobility	Yield Value Deg. Deflection
Short carbon black plus linseed oil	15.0	0.067	59
Long carbon black plus linseed oil	15.3	0.065	23
Lampblack plus linseed oil........	22.0	0.046	33
Raw linseed oil................	3.4	0.019	0

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[1] THIS JOURNAL, 7 (1915), 961.

[1] "Paint, a Plastic Material and Not a Viscous Liquid," Reprint, American Society for Testing Materials, 22nd Annual Meeting, June 24–27, 1919.

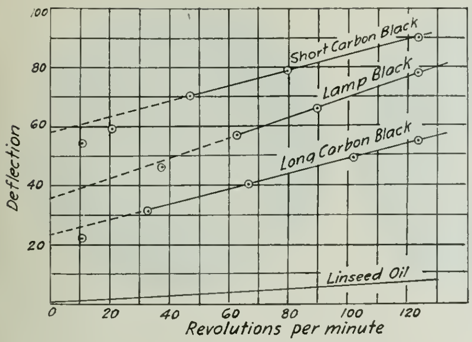

FIG. 1—"VISCOSITY" OF MIXTURES OF BLACK AND LINSEED OIL USING MACMICHAEL TORSION VISCOSIMETER

DISCUSSION OF RESULTS—It is at once seen both from the table and the curves that the difference between the long and short blacks tested is a difference principally in yield value, and that the mobilities of the two mixtures are nearly the same. The lampblack, with a steeper slope, has a lower mobility and a yield value intermediate between the long and short blacks.

The yield value is apparently the resistance, due probably to attractive forces between the particles of black, which the mixture offers to deformation when the load is applied above a certain rate. If the load is applied slowly, a different condition obtains, as instanced by the falling off of the curve from a straight line at the lower speeds of revolution. If the rotation of the cup is stopped while a mixture is being tested, the deflection drops back quickly to a point near the yield value, and then very slowly decreases nearly to zero over a period of several minutes.

It is hoped to continue work with the torsion viscosimeter and to compare results as obtained with it to the results obtained by the capillary method. Results are, of course, empirical, but might nevertheless be of practical value.

COHESION—Cohesion is defined as the attraction between the particles of the same substance. It is the resistance which a substance offers to deformation. An ink with low cohesion is a long ink, *i. e.*, it allows itself to be changed in shape and easily drawn out into strings. One with higher cohesion offers greater resistance to deformation and breaks off when an attempt is made to draw it out into a string with the palette knife.

Cohesion may be measured by determining the force necessary to draw a flat, circular plate away from the surface of the liquid on which it is resting. In order to get duplicable results with a mixture such as ink, the force must be applied quickly. If it is applied slowly, the same indefinite results are obtained as in the viscosity determinations at the lower speeds, due probably to slippage. Results of a few measurements of this character with long and short black mixtures show long blacks to have lower cohesion.

ADHESION—The molecular attraction between the surface of bodies in contact is called adhesion. The adhesion of an ink for the type and paper must influence its working qualities. This is what the printer calls "tack."

Adhesion of a liquid may be measured by dipping a weighed metal plate in the liquid, allowing it to drain at a constant temperature, and reweighing. For a plastic material, such as ink or paint, the value for the adhesion so obtained would probably be modified by the yield value of the mixture.

In making any tests of mixtures of carbon or lampblack in oil, care must be taken that the black is thoroughly incorporated with the oil if duplicable results are to be obtained. The mixture should be thoroughly ground in a paint mill or three-roller ink mill. An inert mineral oil will probably be better than linseed oil for testing purposes.

CHEMICAL ANALYSIS—Carbon blacks consist of from 85 per cent to 95 per cent amorphous carbon, 1 per cent to 7 per cent water, 0.5 per cent to 0.8 per cent hydrogen, and from 2 per cent to 8 per cent oxygen, present partly as CO and CO_2, and partly as fixed oxygen. Chemical analysis serves to show in a general way whether a carbon black will give a long or short ink. A black giving a long ink is usually low in carbon, and high in volatile matter and oxygen, while shorter blacks are correspondingly lower in the latter and higher in carbon. Typical analyses of long and short blacks are given in Table II.

TABLE II—ANALYSES OF CARBON BLACKS

CHARACTER NUMBER OF SAMPLE	Long Black 1	Long Black 2	Long Black 3	Short Black 1	Short Black 2	Short Black 3
PROXIMATE ANALYSIS:						
Moisture	3.56	7.13	5.30	2.25	3.02	3.12
Vol. Matter	11.99	13.41	10.40	5.60	5.48	5.58
Fixed Carbon	84.40	79.44	84.16	92.13	91.47	91.22
Ash	0.05	0.02	0.14	0.02	0.03	0.08
ULTIMATE ANALYSIS:						
Hydrogen	1.19	1.32	1.11	0.74	0.88	1.05
Carbon	88.17	84.56	87.98	94.78	93.50	93.63
Nitrogen	0 04	0.04	0.08	0.09	0 04	0.05
Oxygen	10 54	14.00	10.68	4.37	5.25	5.19
Sulfur	0.01	0.06	0.01	0.00	0.30	0.00
Ash	0.05	0.02	0.14	0.02	0.03	0.08
ULTIMATE ANALYSIS (Moisture-free):						
Hydrogen	0.82	0.57	0.55	0.50	0.52	0.72
Carbon	91.42	91.05	92.91	96.96	96.41	96 64
Nitrogen	0 04	0.04	0.08	0.09	0.04	0.05
Oxygen	7.66	8.26	6.30	2.43	2.69	2.51
Sulfur	0.01	0.06	0.01	0.00	0.31	0.00
Ash	0.05	0.02	0.15	0.02	0.03	0.08

ADSORBED GASES—Carbon black contains considerable quantities of carbon monoxide, carbon dioxide, and oxygen. The oxygen is probably present as "fixed oxygen," that is, in some kind of combination with the carbon. Through the coöperation of Dr. G. A. Hulett and H. E. Cude, of Princeton University, the nature and amount of the adsorbed gases were determined. The apparatus used was that designed by Dr. Hulett to determine the nature of the adsorbed gases in gas-mask charcoal. The gases are pumped off at any desired temperature by means of a Topler pump and analyzed, the water being caught on a bulb containing solid carbon dioxide.

At room temperature the composition of the gas which can be pumped off is practically that of air and the volume about that of the voids and capillary spaces. At 445° C. a larger volume usually comes off, consisting chiefly of CO_2, CO, and N_2. Carbon dioxide may be present in as large amount as one per cent of the

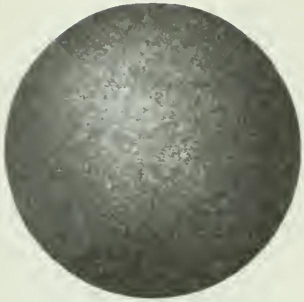
FIG. 2—SHORT BLACK, 18 MIN. AFTER PREPARATION ON SLIDE. MAGNIFICATION 500 DIAMETERS

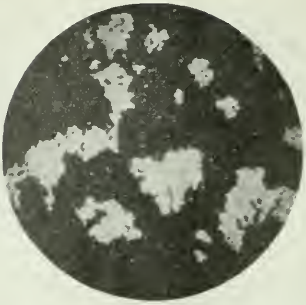
FIG. 3—SHORT BLACK, 2 HRS. AFTER PREPARATION ON SLIDE. MAGNIFICATION 500 DIAMETERS

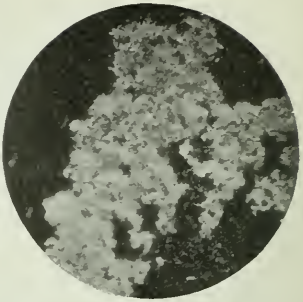
FIG. 4—SAME AS FIG 2. MAGNIFICATION 2000 DIAMETERS

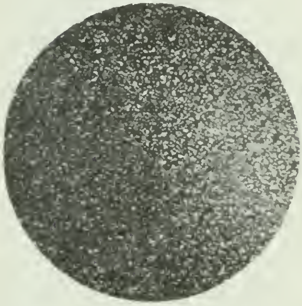
FIG 5—LONG BLACK, 2 HRS. AFTER PREPARATION ON SLIDE. MAGNIFICATION 500 DIAMETERS

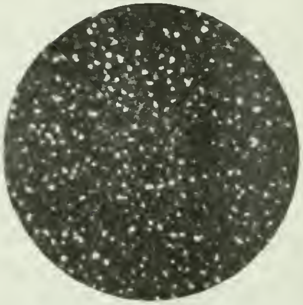
FIG. 6—LONG BLACK, 4 HRS. AFTER PREPARATION ON SLIDE. MAGNIFICATION 2000 DIAMETERS

weight of the moisture- and gas-free black; oxygen about 0.01 per cent; CO, 0.1 to 0.2 per cent; methane and hydrogen, a trace; nitrogen, 0.05 to 0.2 per cent. An insufficient number of samples was analyzed to allow conclusions to be drawn in regard to the relation between adsorbed gases and physical and chemical properties. At the temperatures investigated, none of the hydrogen indicated by the ultimate analysis was pumped off. The carbon dioxide evolved would account for only part of the oxygen shown to be present by the ultimate analysis.

HYGROSCOPICITY—Carbon blacks absorb a considerable amount of moisture when exposed to damp air. Too large a moisture content is detrimental to the working qualities of the black in ink. Blacks containing a high percentage of volatile matter, *i.e.*, long blacks, are as a rule more hygroscopic than are those containing a lesser amount of volatile matter. Table III shows the results of exposing weighed amounts of different blacks over water and over sulfuric acid at a temperature of about 25° C. The blacks when initially weighed were in equilibrium with a humidity of about 60 per cent at 25° C.

TABLE III—HYGROSCOPICITY OF CARBON BLACK

SAMPLE	Percentage Loss in Weight over H_2SO_4 24 Hrs.	72 Hrs.	Percentage Gain in Weight over H_2O 24 Hrs.	72 Hrs.	Moisture at 105° C.
Long Black 1	3.9	4.2	4.9	10.3	3.6
Long Black 2	6.2	6.9	7.0	14.1	7.1
Short Black 1	2.4	2.6	3.1	6.7	2.3
Short Black 2	2.2	2.5	3.6	7.7	3.0

MICROSCOPIC EXAMINATION—According to the ink makers, carbon blacks exhibit a wide range of properties,[1] depending on the method of manufacture.

Apparently a pigment which gives a long ink is one which affects the original properties of the vehicle to a less extent than an equal weight of a short pigment. At first sight this would seem to be merely a question of fineness of subdivision and it is probable that such is the case to a large extent. The tendency of the particles to form agglomerates may also play a part.

We have examined a large number of carbon blacks under the microscope at magnifications as high as 2000 diameters. The particles are very small, below the resolving power of the microscope. Indications are that the average size of the particles of carbon black is about 100 millimicrons. Microscopic examination indicates that the particles of long blacks are slightly larger than those of short blacks, although the apparent difference in size may be due to the effect of different surface conditions on the diffraction of light. Time has not been available to make exact measurements of the size.

Dark ground illumination with the ultra condenser has been found to be the most satisfactory method of examination for most purposes. Examination by transmitted light in the ordinary manner does not distinguish between single particles and small agglomerates of particles. Examination by transmitted light is of advantage in showing up large agglomerates or particles of grit and serves to show the relative opacity of the blacks. In general, the higher the percentage of carbon in a black, the blacker it looks under the microscope. Well calcined lampblacks are more opaque than carbon black or lampblacks containing much volatile matter.

Under the microscope freshly prepared mixtures of thin lithographic varnish and short or long carbon black look at first precisely similar. They consist of ultraparticles or agglomerates of two or three particles. After a few minutes, however, a decided difference is apparent. The short black has begun to agglomerate into groups of 20 or 30 particles and in an hour over 100 may be grouped together. These agglomerates are loosely held together and may be dispersed by pressing down on the cover glass but they come together again in a few minutes. The long black, on the contrary, remains completely dispersed after several hours. Fig. 2 shows a short black 18 min. after preparation on the slide, Fig. 3 shows the same black after 2 hrs., Fig. 4 is a duplicate of Fig. 3, magnified 2000 diameters. Figs. 5 and 6 show a long black after several hours, magnifications 500 and 2000, respectively. The concentration of black in oil on the slide is about 1 part black to 1,000,000 parts oil.

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[1] Underwood, "The Chemistry and Technology of Printing Inks."

Long blacks are usually made with cylindrical burners, a cool flame which tends to produce a black high in volatile matter. It seems probable that these adsorbed impurities prevent the carbon particles from agglomerating. In support of this, we have found that if a long black be treated with steam at 500° C. so that the occluded matter is burned off, the black forms a distinctly thicker mixture in oil and is seen to be agglomerated under the microscope. Conversely, if a definite quantity of a short black be treated with a dilute alcoholic solution of tannin and mixed with oil after the alcohol has evaporated, it makes a much more fluid mixture than an equal amount of untreated black. Under the microscope the tannin-treated mixture is found to be completely dispersed and to show no tendency to agglomerate.

To summarize, blacks which give long ink probably consist of slightly larger particles than those which make a shorter ink, hence exposing less surface per unit weight and taking less oil to form a mixture of given consistency. Furthermore, the difference in surface conditions due to the fact that long blacks contain a high percentage of adsorbed gases, probably influences the properties of the mixture of the black with oil. Microscopic examination of dilute mixtures of black and oil shows one effect of this difference in surface conditions, namely, the tendency of the blacks containing little adsorbed impurities to agglomerate, while the blacks containing large amounts of volatile matter remain dispersed.

SUMMARY

It has been pointed out that although the present process of making carbon black recovers only a few per cent of the carbon in the gas, no other process in practical operation produces a material with similar properties. Inability to secure carbon black would prove a serious blow to the printing industry and would probably inconvenience rubber manufacturers and others. In view of the diminishing supply of natural gas, developmental work on more efficient methods of production and production from other materials is needed. The problem is not an easy one. Developmental work should probably be directed toward the investigation of entirely new methods, such as the thermal decomposition of gas or other hydrocarbons in absence of air, or explosion with CO, CO_2, O_2, or their mixtures.

The uses of carbon black have been discussed, test methods outlined, and a brief account given of preliminary work on microscopic and chemical differentiation of blacks giving long and short inks.

ACKNOWLEDGMENTS

We wish to express our appreciation of the valuable assistance and suggestions of Mr. A. C. Fieldner under whose supervision the work was carried out. We appreciate very much the assistance of Mr. J. O. Lewis, Chief Petroleum Technologist of the Bureau of Mines, and of Mr. R. O. Neal, Chemical Engineer in the Bureau of Mines, who made it possible for one of us to visit carbon black plants in Oklahoma and West Virginia.

THE PRODUCTION OF AMMONIA AND FORMATES FROM CYANIDES, FERROCYANIDES, AND CYANIZED BRIQUETS[1]

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Received September 30, 1919

The hydrolysis of the cyanides of the alkali or alkaline earth metals by steam, whereby ammonia and formates are produced in accordance with the equation

$$MCN + 2H_2O = NH_3 + HCOOM,$$

has been known for a long time and was employed on a commercial scale at least as early as 1843.[2] In the past, however, the great demand for cyanides, and their value as compared with ammonia, have prevented this method from achieving any degree of commercial success. Three pounds of sodium cyanide are required for the production of one pound of ammonia, hence it is obvious that this method cannot compete successfully with the extraction of ammonia from gas liquor unless sodium cyanide can be procured very cheaply.

In recent times the great demand for nitrogen products, and their increased cost, has again directed attention to the hydrolysis of cyanides as a means of obtaining ammonia. Especially in the process of nitrogen fixation[3] with coke and soda ash in the presence of iron (the present success of which is in large measure due to Bucher,[4] who for the first time accurately analyzed the controlling factors), the subsequent hydrolysis of the cyanized briquetted product offers attractive possibilities, since the reaction products might be returned directly to the process, and the expense and difficulty of lixiviation and cyanide recovery avoided.

[1] The work described in this paper was done under the auspices of the Research Section, Nitrate Division, Ordnance Department, U. S. A., at Saltville, Va. Published by permission of Chief of Ordnance.

[2] By Newton, in England. T. H. Norton "Utilization of Atmospheric Nitrogen," Dept. of Commerce and Labor, Bur. of Manufacturers, Special Agents Series, *Bulletin* **52** (1912) See also Thorpe, "Dictionary of Applied Chemistry," **2**, 599, in which reference to original literature and patents is made.

[3] Margueritte and Sourdeval, Eng. Patent 1,027 (1860).

[4] J. E. Bucher, THIS JOURNAL, **9** (1917), 233; *Met. & Chem Eng.*, **16** (1917), 315, *Trans. Am. Inst. Chem. Eng.*, **9** (1916), 135.

Since the data available on the hydrolysis of cyanides are meager, especially as regards details of manipulation, most favorable conditions of temperature and pressure, and yields to be secured, a series of experiments was undertaken on the steaming of sodium cyanide, sodium ferrocyanide, and cyanized briquets. Work was limited to variations of pressure, partly because it was known that the effect of temperature was being studied elsewhere; partly because we believed that increased pressure would give improved yields. The equation for the reaction indicates that there is an actual shrinkage in volume during hydrolysis, two volumes of steam being absorbed for every volume of ammonia formed; hence pressure might be expected to exert favorable influence on the course of the reaction.

Fortunately, the results of the work on the effect of varying temperatures have been made available to us and are summarized and discussed in this report.

EXPERIMENTAL PART

APPARATUS—All hydrolysis experiments were conducted in autoclaves made of 4-in. wrought iron pipe, large enough to accommodate a charge of a kilogram of material and a liter of water. The form of apparatus finally adopted is shown in the accompanying diagram (Fig. 1). For a number of experimental runs at less than 150 lbs. pressure, no water was added, steam being introduced directly from plant boilers through a quarter-inch pipe entering near the bottom of the autoclave. In any case the autoclave was immersed in a bath of cylinder oil, kept above the reaction temperature, to obtain the desired pressure when water was used inside the autoclave, and to prevent condensation of water when steam was introduced.

Pressures were read on a Schaeffer and Budenberg ammonia gauge, reading directly to 300 lbs., and temperatures were recorded by means of ordinary laboratory thermometers immersed in the oil bath, and in some experiments by a mercury-in-iron thermometer (not shown in Fig. 1) inserted near the top of the autoclave.

MANIPULATION—To make an experimental run, the oil bath was brought to the temperature (determined by experiment) required to heat the autoclave to a point corresponding to the desired pressure. The autoclave was then immersed and connected through a quarter-inch union to the condenser. When the desired temperature and pressure had been reached, ammonia (together with any excess steam or other gases) was drawn off through an iron ammonia valve into a water-cooled iron condenser, thence into a barrel or large bottle of dilute sulfuric acid, and determined by titration of the sulfuric acid solution. Titrations were made at frequent intervals in order to follow the course of the reaction.

ANALYTICAL METHODS—All cyanogen compounds used, including the briquets, were analyzed for cyanide content by the method of Lundell and Bridgman[1] in which the cyanide solution or extract is titrated in a solution made slightly alkaline with ammonia against standard nickel ammonium sulfate solution, using dimethylglyoxime as an indicator.

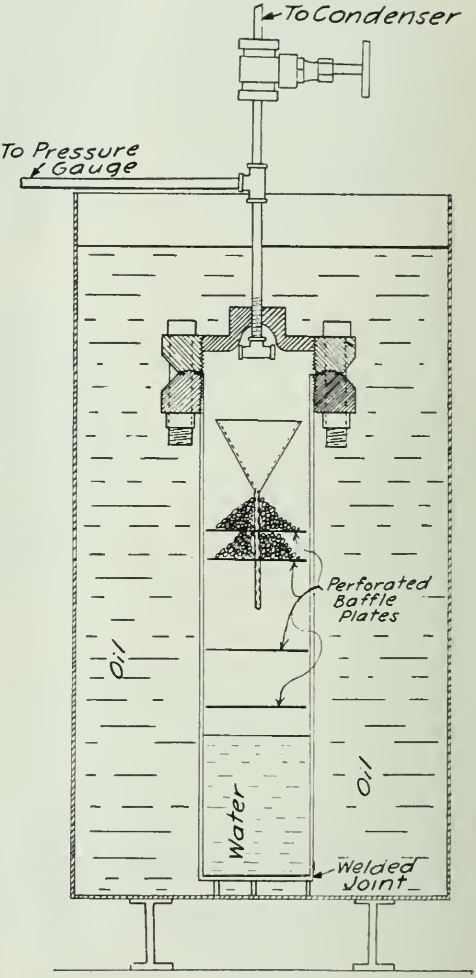

FIG. I

Formates were determined in the usual manner by titration with permanganate in warm alkaline solution.[1]

EXPERIMENTAL DATA

A—*Experiments with Sodium Cyanide*

The following results were obtained by passing steam over sodium cyanide at pressures of 50-80 lbs.

Expts. 1 and 2 are summarized in Table VI.

Expt. 3—The analyses of the reaction mass before and after treatment are given in Table I.

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[1] THIS JOURNAL, 6 (1914), 554.

[1] Lieben, *Monatsh.*, 14, 746; 16, 219.

TABLE I—ANALYSIS OF CYANIDE MASS

	Before Hydrolysis	After Hydrolysis
Sodium cyanide	80.77 per cent	0.07 per cent
Sodium cyanate	5.22 per cent	..
Sodium formate	..	91.96 per cent
Sodium oxalate	.	Nil
Weight	111 g.	130 g.

Expt. 4—The autoclave smelled strongly of ammonia at the end of the run, and there were other indications that the hydrolysis was proceeding as long as water was present, and that better results would have been achieved had more water been present. The analyses before and after hydrolysis are given in Table II.

TABLE II—ANALYSIS OF CYANIDE REACTION MASS

	Before Hydrolysis	After Hydrolysis
Sodium cyanide	83.9 per cent	8.58 per cent
Sodium cyanate	1.99 per cent	..
Sodium formate	..	90.6 per cent
Weight	115 g.	135 g.

B—Experiments with Sodium Ferrocyanide

Because of the possibility of and tendency toward ferrocyanide formation in cyanized briquets, and the resulting decreased yield of ammonia on hydrolysis, Expts. 5 to 11, inclusive, were undertaken on the steaming of sodium ferrocyanide.

Expts. 5 and 6 are summarized in Table VI.

Expt. 7—The foregoing attempts to hydrolyze ferrocyanide having resulted in virtual failure on account of frothing, the effect of the addition of sodium hydroxide was studied with the result noted in Table VI.

Expt. 8—In spite of all precautions, frothing occurred after 2 hrs. when 27.1 per cent of the theoretical yield of ammonia had been produced.

Expt 9—A pressure of 300 lbs. developed in 2 hrs. The hydrolysis was terminated before its completion because the water entirely distilled out of the autoclave while the reaction was still in progress.

Expt. 10—To continue experiments on the effect of alkalies, lime was used. A partial analysis of the reaction product is given in Table III.

TABLE III—ANALYSIS OF REACTION PRODUCT FROM FERROCYANIDE HYDROLYSIS

	Per cent
Sodium ferrocyanide	28.8
Formate (as HCOONa)	12.8
Lime (CaO)	13.8

Expt. 11—In a similar run where sodium carbonate was employed, the reaction product gave the following analysis:

TABLE IV—ANALYSIS OF REACTION PRODUCT FROM FERROCYANIDE HYDROLYSIS

	Per cent
Sodium ferrocyanide	44.3
Sodium carbonate	23.7
Formate (as HCOONa)	28.5

The foregoing experiments show that cyanide can readily be hydrolyzed at comparatively low pressure, and that ferrocyanide is acted upon slowly and with difficulty. Alkalies, other than perhaps caustic soda, did not greatly affect ferrocyanide decomposition.

C—Experiments with Cyanized Briquets

The briquets were obtained from U. S. Chemical Plant, Saltville, Virginia. Preliminary experiments showed that good yields of ammonia cannot be obtained from cyanized briquets at 50 lbs. steam pressure, the reaction products being essentially ferrocyanide and hydrogen.[1] It was found further that, though some hydrogen was also formed at 120 to 150 lbs. pressure, good yields of ammonia could be secured.

Expts. 12 and 13 are sufficiently well described in Table VI.

Expt. 14—In this experiment the ferrocyanide content rose from 8 per cent in the original mixture to 10 per cent in the residue, the increase corresponding to a formation of approximately 10 g. of sodium ferrocyanide during the reaction. No oxalate was detected in the residue. Sodium formate, 93 per cent pure and free from carbonate, was recovered from the residue by extraction.

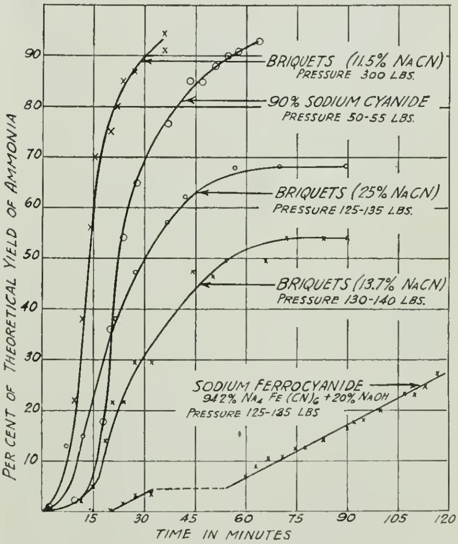

FIG. 2—HYDROLYSIS OF SODIUM CYANIDE, FERROCYANIDE, AND CYANIZED BRIQUETS

Expt. 15 requires no special comment.

Expt. 16—The routine analytical results from the briquets before and after treatment are given in Table V.

TABLE V—ANALYSIS OF BRIQUETS

	Before Steaming Per cent	After Steaming Per cent
Sodium cyanide	11.2	0.0
Sodium cyanate	0.4	Trace
Sodium carbonate	23.87	29.16
Sodium ferrocyanide	1.38	0.16

The experimental results are summarized in Table VI, and typical runs are shown graphically in Fig. 2.

DISCUSSION OF RESULTS

For comparative purposes the results obtained with

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[1] C. F. Bierbauer and L. S. Finch, U. S. Patents 1,295,262 and 1,295,293, *Met. & Chem. Eng.*, **20** (1918), 431, attempt to obviate this difficulty by dissolving crude cyanide as rapidly as possible by blowing pulverized briquet material into a tank equipped with water spray and agitator, rapidly filtering the mixture, and heating the solution with steam under 125 lbs. pressure, the ammonia being allowed to escape through a relief valve set at 50 lbs.

TABLE VI—HYDROLYSIS OF SODIUM CYANIDE, SODIUM FERROCYANIDE AND CYANIZED BRIQUETS

Expt. No.	Charge	Time Min.	Steam Pressure in Autoclave Lbs.	Temperatures ° C.			Ammonia Yield Per cent of Theoretical	Remarks
				Corresponding to Steam Pressure	Recorded	Oil Bath		
	SODIUM CYANIDE							
1A	90 per cent NaCN, 300 g.	80	70–80	158–161	140–155	165–175	65	Charge frothed into condenser, stopping run
2A	90 per cent NaCN, 150 g.	65	50–55	148–150	145–148	210	93	Charge frothed into condenser, stopping run
3B	83 2 per cent NaCN, 111 g.	60	200 (Av.)	185–210	...	215–220	100	500 cc. water in autoclave
4B	85.5 per cent NaCN, 115 g.	120	55	150	...	210	82	1000 cc. water in autoclave. Reaction proceeded until autoclave was dry
	SODIUM FERROCYANIDE							
5A	$Na_4Fe(CN)_6.10H_2O$, 500 g.	30	120–135	170–181	180	160–200	Trace	Frothing put end to run
6A	94.25 per cent $Na_4Fe(CN)_6$, anhyd., 310 g.	70	120–135	170–181	180	220–240	Little	Frothing, pronounced odor of NH_3 at end of run
7A	94.25 per cent $Na_4Fe(CN)_6$, anhyd., 150 g. + 30 g. NaOH	80	125–145	173–184	180–185	200	17	Frothing, pronounced odor of NH_3 at end of run
8A	94.25 per cent $Na_4Fe(CN)_6$, anhyd., 150 g. + 35 g. NaOH	120	125–135	178–181	178	225	27.1	Frothing, pronounced odor of NH_3 at end of run
9B	96.5 per cent $Na_4Fe(CN)_6$, anhyd., 52 g.	285	300–330	220	. .	250	46.6	800 cc. water in autoclave
10B	90.5 per cent $Na_4Fe(CN)_6$, anhyd., 106 g. + 25 g. CaO	112	300–330	220	...	250	15.8	1000 cc. water
11B	96 per cent $Na_4Fe(CN)_6$, anhyd., 35 g. + 15 g. Na_2CO_3	170	300–340	220	. .	260	25.3	1000 cc. water
	CYANIZED BRIQUETS							
12A	Powder, 23.5 per cent NaCN, 440 g.	55	135	180	180	. .	50	Charge frothed into condenser
13A	Briquets, 13.7 per cent NaCN, 730 g.	72	130–140	180–183	175–178	220	54	Hydrogen formed
14A	Powder, 23.5 per cent NaCN, 400 g.	60	125–135	178–181	174–177	220	68	Residue free from cyanide
15B	Briquets, 13.8 per cent NaCN, 750 g.	38	300	220	...	230	90.7	500 cc. water in autoclave Briquets recovered unbroken
16B	Briquets, 11.5 per cent NaCN, 1000 g.	41	300–330	220	...	240	92.5	700 cc. water Good briquets recovered

In experiments marked "A" steam was passed into autoclave; in those marked "B" water was introduced directly.

superheated steam at atmospheric pressure are briefly summarized in Table VII.[1]

TABLE VII—STEAMING EXPERIMENTS AT ATMOSPHERIC PRESSURE—PERCENTAGE OF THEORETICAL AMMONIA PRODUCTION

Material	200° C.		300° C.		400° C.		500° C.		600° C.	
	Per cent	Time. Hrs.	Per cent	Time. Hrs.	Per cent	Time. Hrs.	Per cent	Time. Hrs.	Per cent	Time. Hrs.
Sodium cyanide	0.8(?)	4	56	6	61	6	73	6	74	6
Sodium ferrocyanide	0.3	4	0.5	6	5	6	88	4	91	4
Briquets, 20.5 per cent NaCN	54	4	57	4	84	6	99	4	100	4
Briquets, 14 7 per cent NaCN	60	4	47	4	79	6	84	4	85	4

It should be pointed out that this work differs essentially from our own in that much smaller quantities of materials were used for hydrolysis; whereas we used from 100 to 1000 g., the work in Table VII was done with amounts ranging from 2 to 10 g. The results of this series indicate that if steaming is done at atmospheric pressure, the temperature must be raised to at least 600° C. to obtain quantitative yields of ammonia. Although the experiments in question were continued for periods of 4 to 6 hrs., the greatest portion of the ammonia was obtained in from 30 min. to one hour.

Using steam under pressure with different degrees of superheating, results were obtained as shown in Table VIII.

TABLE VIII—EXPERIMENTS WITH STEAM UNDER PRESSURE

Gauge Pressure (pounds)...	—0—		—25—		—50—		—75—		—100—	
	Per cent	Time. Hrs.	Per cent	Time. Hrs.	Per cent	Time Hrs.	Per cent	Time. Hrs.	Per cent	Time. Hrs
Briquets, 20.5 per cent NaCN (saturated steam)	12	3.5	25	4	30	4	36	4	44	4
Briquets, 20.5 per cent NaCN. Reaction at 300° C.	56	4	61	4	70	4	80	4	86	4
Briquets, 20.5 per cent NaCN. Reaction at 400° C.	75	4	83	4	93	4	100	4	102	4

The above data indicate that with a steam pressure of 100 lbs., a temperature of at least 400° C. must be maintained to secure quantitative yields of ammonia. Our own work indicates that the exceedingly high temperatures noted above are not necessary for the hydrolysis of cyanides on a commercial basis. We have found that a pressure of 300 lbs. without superheat will insure satisfactory results.

The hydrolysis of cyanides may be accomplished without great difficulty at temperatures and pressures which can readily be secured in commercial practice. The reaction proceeds more rapidly at high steam pressure than at low, as might be expected. That pressure and not merely the higher temperature of compressed steam is a deciding factor is proved by the fact that much higher temperatures are required for hydrolysis at atmospheric pressure than those recorded in the present work.

A possible advantage of work at the comparatively low temperatures here recorded arises from the fact that hydrolysis proceeds without indications of side reactions, virtually quantitative yields of formate being secured. The available literature indicates that there is little danger of decomposition of formates below 200° C. Above this temperature oxalates might be formed, and at still higher temperatures oxalates decompose to form carbonates. (The temperature of saturated steam at 300 lbs. pressure is 217° C.)

In runs made at the same pressure, better results were secured by passing steam into the autoclave than by introducing water direct. This is to be expected, since, in the former case, fresh steam comes in contact with the reaction mass.

The experiments with ferrocyanide showed that hydrolysis takes place very slowly, even at 300 lbs. steam pressure. Results were not materially benefited by the addition of alkalies, though at a pressure of 125 lbs. the addition of caustic soda gave indications of an increased yield.

The hydrolysis of cyanized briquets to form ammonia does not proceed very far at low pressures, the best yield obtained at 125 lbs. being only 68 per cent.

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[1] The data in Tables VII and VIII were obtained by Mr. J. A. Beattie of the Nitrate Division, working in the Geophysical Laboratory.

This is due, in a large measure at least, to the formation of ferrocyanide, probably as follows:

$$Fe + 2H_2O = Fe(OH)_2 + H_2 \quad (1)$$

$$Fe(OH)_2 + 6NaCN = Na_4Fe(CN)_6 + 2NaOH \quad (2)$$

The formation of ferrocyanide, which takes place readily enough, seemed further to be influenced appreciably by the sulfur content of the briquets, in accordance with the reaction:

$$6NaCN + FeS = Na_4Fe(CN)_6 + Na_2S \quad (3)$$

At low pressures the formation of ferrocyanide in briquets seems to progress more rapidly than its decomposition, so that the ferrocyanide content materially increases, as shown in Expt. 13. It is therefore clear that to obtain a maximum yield, ammonia should be liberated from the cyanide as rapidly as possible, preferably at a temperature and pressure at which ferrocyanide is hydrolyzed with appreciable velocity. These conditions were obtained in Expt. 16, in which a maximum yield (92.5 per cent) of ammonia was obtained, and in which the ferrocyanide content was actually decreased. The good results obtained at 300 lbs. indicate the desirability of working at this pressure. It does not seem advisable to go much higher in commercial operation.

Bierbauer and Finch[1] describe a procedure whereby, in the presence of much ferrocyanide, all the cyanide in the pulverized briquet mass is converted into ferrocyanide by digestion with finely divided iron, whereupon the mass is filtered, and hydrolyzed at 80 to 150 lbs. steam pressure. In our own work we were unable to secure satisfactory yields of ammonia by steaming ferrocyanide at such low pressures.

If condensation in the autoclave is prevented, briquets may be steamed without physical disintegration, and can be returned to the cyanizing retorts. It has been shown from previous experiments that at the cyanizing temperature of 950° to 1000° C., carbon monoxide (formed in this case by the decomposition of formates to carbonates) does not interfere in any way with the nitrogen fixing reaction. It is believed that briquets could be put through the process three times without disintegration, so that a great saving in the cost of briquetting would be effected. It is clear also that unless sodium formate (or oxalate) is to be recovered there is no very apparent advantage to be derived from the use of soda ash as one of the raw materials for the cyanizing process. Barium compounds would naturally suggest themselves because of the relative ease with which they fix nitrogen,[2] and even calcium compounds might be applicable.

Although no appreciable temperature effect was noted in the present work, the fact that the reaction is strongly exothermic might prove advantageous both by reducing the amount of heat to be supplied from without and by tending to prevent condensation of moisture which causes the briquets to stick together or disintegrate. On the other hand, a very considerable rise in temperature might induce secondary reactions such as the conversion of formate to oxalate and of the latter to carbonate. It is also possible that the ammonia might be partially decomposed by being heated in contact with finely divided iron, a reaction which begins at about 500° C., though the results of high temperature experiments quoted above do not corroborate this view.

It is believed that the actual cost of the process of making ammonia from cyanide is low. Whether it can be made profitably depends largely on the cost of cyanide in the iron-coke briquet mass. In any case, at least three times the cost per pound of cyanide in the briquets would have to be added to the cost of the process, since 3 lbs. of cyanide are required for the production of one pound of ammonia. For example, assuming that cyanide in the iron-coke mass costs 10 cts. per lb., and that the cost of ammonia production is 4 cts., the total cost of the ammonia would be 34 cts. if the formate formed were not recovered.

Two dispositions may be made of the formate: it may be left in the briquets and returned to the process, or it may be extracted and recovered if market conditions warrant. There are certain advantages to be gained from the first course. If the briquets are kept dry during the steaming, they are obtained at the end of the process in good condition and may be returned directly to the cyanizing process. They can probably be passed through the complete cycle three times before it is necessary to rebriquet them. As far as cyanide formation is concerned, formates would be equivalent to carbonate because the former could be converted into the latter on heating. Thus, the entire cost of the fresh sodium carbonate otherwise necessary, and one-half to two-thirds of the cost of kneading, briquetting, and drying, would be eliminated.

If the formate is to be returned to the process, the whole process might be cheapened somewhat by the substitution of barium or possibly calcium for sodium in the manufacture of cyanide. Margueritte and Sourdeval used barium carbonate, carbon, and iron, and state that barium compounds react with nitrogen much more readily than potassium compounds (and presumably more readily than sodium compounds). Thus not only might the process of cyanide formation be cheapened through the use of cheaper material, but it might also be made more efficient, either by lowering the temperature of the reaction or increasing the yield, or both. This suggests some interesting possibilities in the way of future experiments on nitrogen fixation along the line of comparison between barium or calcium and sodium compounds under the same conditions.

On the other hand, the formate may be recovered in fairly pure form by lixiviating the steamed reaction mass with alcohol. It may also be obtained at less cost, but in cruder form, by lixiviation with water. The formates might be used as a starting point for other compounds, such as esters, formic acid, oxalates, or oxalic acid.

SUMMARY

The formation of ammonia from sodium cyanide, sodium ferrocyanide, and cyanized briquets was

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[1] *Loc. cit.*

[2] Margueritte and Sourdeval, *Loc. cit.*

studied. Good yields of ammonia were obtained from sodium cyanide by steaming at 50 lbs. pressure. A quantitative yield was obtained at 200 lbs.

The hydrolysis of ferrocyanides proceeded very slowly. A maximum yield of 46 per cent was obtained by steaming $4^3/_4$ hrs. at a pressure of 300 to 330 lbs.

With cyanized briquets, yields averaging over 90 per cent were obtained in 30 to 45 min. by steaming at 300 to 330 lbs.

To obtain satisfactory results with steam at atmospheric pressure, a temperature of 600° C. was necessary.

High temperatures were necessary to obtain good results with steam at low pressure. A temperature of 600° C. with atmospheric pressure and 400° C. with 100 lbs. pressure gave satisfactory results.

At the temperatures involved in the experiments with saturated steam there were no indications of side reactions, only formates and ammonia being produced.

THE PREPARATION OF HEXANITRODIPHENYLAMINE AND ITS USE AS A BOOSTER FOR SHELL CHARGES[1]

By John Marshall

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Early after the entry of the United States into the war it became evident that the country's capacity for the manufacture of secondary detonating materials or "booster" explosives for high explosive shells was insufficient to provide for the extensive program planned by the Ordnance Department.

The material which had been used to the best advantage for this purpose and the one apparently preferred above all others was tetryl, or tetranitromethylaniline. Closely approaching this compound in value was tetranitraniline, though the latter had some disadvantages connected with its use on account of its questionable stability in the presence of moisture.

It was evident therefore that in order to compete with these compounds and at the same time supplement the available supply of secondary detonating agents, it would be necessary to produce a material of similar properties, *i. e.*, high melting point, sensitiveness to detonation, and power as a detonator, and at the same time to produce it by some method whose simplicity would make it possible to compete with the relatively low prices of tetryl and TNA. Added to these requirements it was considered necessary to develop such a compound from sources other than toluene in order to conserve as far as possible the supply of this material.

A survey of the field indicated that the symmetrical hexanitrodiphenylamine would probably meet these requirements, though the literature was singularly vague on the properties of the material. A careful study was therefore made early in 1918 on the manufacture and properties of this compound. The results in a large measure justified the hopes which had been felt, and it is probable that had the war continued, hexanitrodiphenylamine, or hexil, as it has been named, would have found a use as a substitute for tetryl in boosters for high explosive shells.

The first description of this compound was given in 1874 by P. T. Austen,[1] who prepared it by nitration of picryl-*p*-nitraniline, and during the same year it was prepared by Gnehm[2] by the nitration of diphenylamine. Neither of these methods can have any practical value on account of the high cost of the intermediates involved.

The synthesis described in a patent of the Chemische Fabrik Griesheim,[3] and elaborated in 1913 by T. Carter,[4] offered greater advantages, and it was this method which was settled on for development. This method as described by Carter depends on the reaction of 1,2,4-chlorodinitrobenzene with aniline to form dinitrodiphenylamine and aniline hydrochloride, with subsequent nitration by nitric acid in two stages to hexanitrodiphenylamine.

It should here be pointed out that a recent article by Messrs. Hoffman and Dame[5] indicates that the Bureau of Mines was also interested in this subject, their work in a measure duplicating the early phases of our own work.

PREPARATION OF DINITRODIPHENYLAMINE

The first preparation of dinitrodiphenylamine was made in accordance with Carter's procedure. This method consists of agitating two molecules of aniline with one molecule of chlorodinitrobenzene, the reaction beginning slowly at moderate temperature. There is at first a slow rise in temperature followed by a more energetic one, which carries the temperature to 125° C., at which point the charge is drowned in water and extracted with water and dilute hydrochloric acid to remove excess aniline and by-product aniline hydrochloride.

In the laboratory excellent results were obtained with theoretical yields of a product melting at 149° to 152° C. When the process was tried on a larger scale, however, it was found difficult to control the temperature properly without drowning the charge before the completion of reaction, since the charge rapidly became so viscous that efficient agitation was out of the question.

The following more satisfactory method was then devised.[6] Two molecules of aniline and one molecule of chlorodinitrobenzene are added to three times their combined weight of water heated to 60° C., and the mixture is agitated mechanically to form an emulsion. Steam is then introduced to raise the temperature to 80° C., the reaction beginning during this heating, and coming to completion in one hour. The dinitrodiphenylamine precipitates in the form of thick clusters of red needles. Agitation at 80° C. is continued one-half hour longer to insure complete solution of aniline hydrochloride, after which the charge is thrown on a filter, washed with dilute hydrochloric acid and water, and finally dried. 95 to 100 per cent of theoretical yields are obtained of material melting at 148° to 152° C. The mother liquor from this process is available for recovery of aniline, and in several runs made in the laboratory recoveries of 85 per cent of the theory were made. This method gave perfect reaction control, and in addition yielded a product in such form that it could be used at once for nitration. Several runs were then made on the 100 lb. scale with equally satisfactory results.

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[1] Presented at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

[1] *Ber.*, **7**, 1248.

[2] *Ibid.*, **7**, 1399.

[3] D. R. P. 86,295, July 1885.

[4] *Z. ges. Schiess-Sprengstoffw.*, **1913**, 205–251.

[5] *J. Am. Chem. Soc.*, **41** (1919), 1013.

[6] U. S. Patent 1,309,580, July 8, 1919.

PREPARATION OF TETRANITRODIPHENYLAMINE

In the nitration of dinitrodiphenylamine thus prepared to the tetra stage, as before stated, the method of Carter involves the addition of dry dinitrodiphenylamine to nitric acid of approximately 40 per cent concentration at temperatures up to 90° C. Any method of nitration involving the use of straight nitric acid is open to serious objections on account of excessive consumption of nitric acid and the necessity for using enameled equipment; and in addition to these objections it was found on trial of Carter's method that the nitration was liable at times to serious and almost uncontrollable foaming.

Carter's article makes the definite statement that a mixed nitric-sulfuric acid cannot be used for this nitration on account of the insolubility of dinitrodiphenylamine in sulfuric acid, but since the claim appeared unreasonable, a series of experiments was instituted on the use of mixed acid for nitration. After considerable investigation it was found that the nitration could be carried out satisfactorily by the addition of dry dinitrodiphenylamine at 70° C. to 3.5 to 4 parts of a mixed acid containing 30 to 45 per cent HNO_3 and 50 to 40 per cent H_2SO_4, followed by raising the temperature to 80° to 90° until evolution of NO_2 was at a minimum. The nitration charge was then cooled and filtered for removal of the spent acid. The product of this nitration was a brownish yellow amorphous material, containing small percentages of higher nitration products, and was found to be in such condition that it could be used directly for the final nitration.

NITRATION OF TETRANITRODIPHENYLAMINE TO HEXANITRODIPHENYLAMINE

Carter's procedure for the final nitration also involves the use of straight nitric acid, tetranitrodiphenylamine being added at 40° to 70° C. to a 90 per cent nitric acid, with final heating at 90° C., followed by cooling and filtration. The product from this method consisted of a finely divided, almost amorphous material which dusted badly, and consequently involved danger of poisoning in handling.

It was found on experimenting that mixed acid could be used with satisfaction at this stage also, and that the character of the product could be varied at will from the amorphous form to the crystalline form by varying the proportion of nitric to sulfuric acid. For example, by the use of a mixed acid containing 25 per cent HNO_3 and 70 to 75 per cent H_2SO_4, an amorphous product was obtained, as compared with a distinctly crystalline product when an acid containing 60 per cent HNO_3 and 40 per cent H_2SO_4 was used. As a crystalline product is the more desirable, an acid of the last noted composition was finally used.

The final procedure consisted of adding the acid tetranitrodiphenylamine to 3.75 parts mixed acid at 70° C., followed by one hour's heating at 90° C., cooling to room temperature and filtering. The product thus obtained was a distinctly crystalline, yellow, free running material, melting sharply with decomposition at a temperature between 238.5° and 239.5° C.

This procedure, for both the tetra- and the hexa-stage nitrations, was also studied thoroughly on the 100 lb. scale, with entirely satisfactory results. Yields of 86 per cent of the theory were obtained, this point duplicating the result of the nitration with straight nitric acid. Spent acid recoveries throughout were very good and the spent acid composition was such that it could be handled in iron. The following are specimen analyses of the spent acid from the two stages:

	TETRA-STAGE SPENT ACID Per cent	HEXA-STAGE SPENT ACID Per cent
HNO_3	14.28	33.62
H_2SO_4	50.95	40.03
$HNOSO_4$	7.45	11.30
H_2O	26.13	14.16
Ether soluble	1.07	0.89

PREPARATION OF HEXANITRODIPHENYLAMINE BY COMPLETE NITRATION OF DINITRODIPHENYLAMINE WITH MIXED ACID

In the article by Hoffman and Dame[1] the possibility is suggested of preparing hexanitrodiphenylamine by a one-stage nitration with mixed acid. This procedure was found to be possible by adding dinitrodiphenylamine to 3.75 parts of a mixed acid containing 60 per cent HNO_3 and 30 per cent H_2SO_4 at temperatures up to 70° to 80° C. This results in the formation of the tetranitro compound. Two parts of fuming acid, analyzing 107 to 108 per cent H_2SO_4 are then carefully added at 80° to 90° C. to bring about nitration to the hexa stage and the charge is cooled after one hour, and filtered. 85 per cent of theoretical yields were obtained of amorphous material melting at 238° C. Cost estimates indicated that the two-stage process was preferable to this method, and it was not pursued further.

In this connection it was found that the use of acids of higher than 90 per cent acidity produced charring of dinitrodiphenylamine.

NEUTRALIZATION OF FREE ACID IN HEXANITRODIPHENYLAMINE

In the work so far discussed no mention has been made of the methods used for freeing the hexanitrodiphenylamine from the free acid carried by the particles of the material.

No alkali can be used with hexanitrodiphenylamine for the reason that the material acts as an acid in the presence of alkalies, forming highly soluble salts, and it is therefore necessary to depend on the use of water for washing. It was found that there was great difficulty in completely purifying amorphous hexanitrodiphenylamine, but that the acid could be completely removed from the crystalline material by means of a drowning wash, followed by 2 or 3 one-hour washes with boiling water, after which the product can be centrifuged and dried on trays at temperatures up to 80° C.

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[1] *Loc. cit.*

EXPLOSIVE PROPERTIES OF HEXANITRODIPHENYLAMINE

While the foregoing work was being carried out on the preparation of hexanitrodiphenylamine, a thorough study was also made of the properties of the material in comparison with tetryl and tetranitraniline, the compounds which it was desired to replace, and with TNT.

The most important properties of an explosive for any purpose are unquestionably stability, sensitiveness to detonation, and explosive power. For use in a booster charge these items are especially important. The stability must be high, because of the high temperatures liable to occur in field service. The material must be sufficiently sensitive to give complete detonation with its primer charge, and, at the same time, must be sufficiently insensitive to eliminate danger from premature explosion. It must also be powerful enough to insure complete detonation of the bursting charge of the shell with a minimum size of booster charge.

As a test for stability, the Abel heat test has for a long time been recognized by the authorities as perhaps the most reliable. During the period of the war, however, the value of this test has been questioned many times when used for nitro compounds, and it is therefore being supplanted by other tests depending on the actual determinations of the products of decomposition of the nitro compound on heating. The most easily applied of this class of tests is the Obermuller, or gas evolution test,[1] and this was developed in our laboratory to a fair degree of satisfaction.

It consists of heating a weighed portion of the material in question at 120° C. *in vacuo* in a calibrated flask attached to a calibrated manometer. Pressure readings are taken every hour on the manometer, the increase in pressure being calculated back to cc. gas evolved per hour at the desired pressure.

Tested in this manner, hexil showed the following results, in comparison with other explosives:

	M. P.	Stability cc. per hr. per g. at 100 mm. pressure
Hexil	140.0	4.4
TNT	77.3	3.6
	80.1	2.1
Tetryl	127.0	13.8
	128.2	2.6
	129.0	1.6

It appears therefore that hexil has a stability close to that of TNT and tetryl, and it may be added that later routine tests on semi-works product indicated a normal stability somewhat better than tetryl of service quality.

SENSITIVENESS OF HEXANITRODIPHENYLAMINE TO DETONATION

The subject of sensitiveness to detonation has fortunately been more thoroughly studied in the past than has the subject of stability, and a number of recognized methods are at hand for this test.

Probably the most reliable of these methods is that in which determination is made of the minimum weight of priming charge to insure complete detonation.[1] This test consists essentially of firing, with varying weights of fulminate-potassium chlorate priming mixture, a series of blasting caps loaded with equal weights of the material to be tested. The lead plate test described by Brunswig[2] was used as an index to completeness of detonation.

The minimum priming charges for complete detonation of the several explosives compared were:

	Gram
Hexil	0.1800
Tetryl	0.2000
TNA	0.2000
TNT	0.2500

These tests showed therefore that hexil is slightly more sensitive to detonation than tetryl and TNA, and in addition indicated that the efficiency of hexil is practically the same as for tetryl and TNA, inasmuch as the perforations in the lead plates from all three compounds were comparable.

SENSITIVENESS TO IMPACT

The foregoing test for sensitiveness to detonation was supplemented by test for sensitiveness to impact and friction in order to gain an idea as to the safety of handling the material. Sensitiveness to impact was determined by the so-called drop test, in which 0.2 g. of explosive, placed on an anvil between two plungers, is subjected to the fall of a 20-kg. weight through a measured distance, the sensitiveness being expressed in terms of maximum height of drop at which no detonation occurred.

In this test, hexil gave no detonation at 5 in., while at the same height tetryl gave one detonation out of 10 trials, TNA four detonations out of 10 trials, and TNT no detonations. Hexil showed detonation at 6-in. drop, but TNT gave none until 25 in. drop was reached. It appears from this that hexil is somewhat less sensitive to shock than tetryl and TNA, and is possibly safer to handle.

SENSITIVENESS TO FRICTION

The sensitiveness to friction was studied in a pendulum friction apparatus such as was developed by the Bureau of Mines.[3] In this test 7 g. of explosive are placed on a bed plate and subjected to the friction of a 20-kg. weight attached to a pendulum swinging from a measured vertical height. Using a steel bed plate and a steel shoe, the pendulum falling from 1.5 meters vertical height and swinging 19 times before coming to rest, hexil, TNT, and tetryl gave no evidence of either local or general detonation. TNA, however, gave some local detonations.

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[1] *J. Am. Chem. Soc.*, **30** (1908), 271.

[1] Bureau of Mines, *Technical Papers* **125** and **145**.

[2] Brunswig, Monroe & Kibler, "Explosives," p. 112.

[3] Bureau of Mines, *Bulletin* **66**, 15.

RIFLE BULLET TEST

As a measure of sensitiveness to impact and friction combined, the rifle bullet test is recognized as most severe. This test consists of packing about 1 lb. of the explosive to be tested into a 3.5-in. cube box of cardboard or tin, and firing into it from a distance of 30 yards with standard U. S. Army rifle (New Springfield). With hexil no detonations were obtained with cardboard boxes, but with tin boxes 7 detonations and one failure were obtained. With TNT no detonations were obtained with cardboard boxes. With tin boxes, the first and second hit in every case set fire to the TNT and the third hit gave a detonation. With tetryl and TNA detonations were obtained with both cardboard and tin boxes.

The preceding results on sensitiveness appeared to indicate that hexil is as sensitive as TNA and tetryl to the action of a primer, but with regard to mechanical shock or friction is more in a class with TNT and is therefore safer to handle.

EXPLOSIVE POWER OF HEXANITRODIPHENYLAMINE

The first tests which are usually applied in a determination of the explosive power of any compound are the ballistic mortar test and the determination of velocity. The ballistic mortar test[1] is widely used and its details are well known. Briefly, the strength is determined in terms of some well-known explosive, for example, TNT, by firing such weights of the two explosives in the ballistic mortar as to give equal swings of the pendulum. Taking the strength of TNT as 10, the following results were obtained:

TNT	10.0
Hexil	11.1
TNA	12.1
Tetryl	12.1

The strength of hexil is therefore midway between that of TNT and tetryl.

A determination of the velocity of detonation of hexil, made by the method of Dautriche,[2] showed a velocity of 6898 m/sec. at 1.58 density, and 7150 m/sec. at 1.67 density.

Similar figures from Marshall[3] for tetryl are:

Density	Velocity
1.53	7075 m/sec.
1.57	7155 m/sec.
1.63	7215 m/sec.

and for TNT, density 1.59 and velocity 6649 m/sec.

It appears, therefore, that in explosive power and velocity, hexil is inferior to tetryl, but superior to TNT.

EFFECT AS A BOOSTER

It having been demonstrated that hexil has a satisfactory sensitiveness and power, it only remains to make a final comparison of hexil and tetryl as secondary detonators in their effect on the bursting charge of a shell. An index was given to this in the lead plate test previously described in which it was found that while somewhat more sensitive than tetryl, hexil did not quite come up to tetryl as a booster material.

More conclusive results were given by a series of tests of the ability of tetryl and hexil, respectively, to detonate insensitive mixtures of TNT and iron oxide. In this test blasting caps were made up of 6.5 grains secondary charge (tetryl or hexil) and 5.3 grains primer (90–10 fulminate-chlorate mixture) and these caps used in firing a series of dynamite cartridges in which different mixtures of TNT and iron oxide had been handpacked. It was found that tetryl would give satisfactory detonation of a mixture containing 14 per cent iron oxide, while the limiting mixture for detonation with hexil contained only 11 per cent iron oxide. While not equal to tetryl as a booster explosive, therefore, hexil shows to good advantage.

A final test of effect as a booster was made in comparison with other booster materials by fragmentation tests on a number of 3-in. base detonating shells.

In this test the bursting charges of the shells consisted of cast refined TNT. Five each of the boosters were loaded with tetryl and TNT and 10 each with hexil and TNA as secondary detonators. The fragmentations were made by dropping the shells from a height of 25 ft. into a steel bomb-proof chamber, the detonation being produced by the striking of the shell on a heavy iron anvil. The fragments were then collected, weighed to obtain percentage of recovery, sorted by sieving, and counted. The average results obtained were as follows:

BOOSTER MATERIAL	TETRYL	TNT	TNA	HEXIL
Wt. booster charge, grams	28	27.5	27.5	27.5
Wt shell charge, grams	478	480	446	450
Wt. of metal in shell, grams	6275	6261	6126	6156
Wt. of material recovered, grams	6108	6116	6096	6112
Per cent of material recovered, total	97.5	97.8	99.5	99.3
Number of fragments on 2 mesh	178	161	188	179
2–4 mesh	1824	1679	1781	1651
4–6 mesh	2002	1840	1969	1830

From these results it appears that hexil is not so good as tetryl or TNA as a booster material, and is more nearly comparable with refined TNT for this purpose. It does, however give a satisfactory order of detonation.

In connection with the use of hexil as a booster it is interesting to make note of the densities given by the compressed material. It was found impossible to make satisfactory blocks by the compression of crystalline hexil alone, but by the addition of 1 to 2 per cent of stearic acid excellent blocks resulted.

Using one per cent stearic acid as a binder, the results were as follows, the absolute density of crystalline hexil being 1.653:

PRESSURE Lbs. per sq. in.	DENSITY
5,000	1.43
10,000	1.56
15,000	1.59
20,000	1.60

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[1] Comey and Holmes, *8th Intern. Congr. Applied Chem.*, **25**, 209.

[2] *Compt. rend.*, **143** (1906), 641.

[3] "Explosives," **1915**, 403.

The best blocks were given by 10,000 lbs. and this was adopted as the standard pressure for preparing pellets for boosters.

CONCLUSIONS

From the work which has been outlined it appears that the following conclusions were justified:

(1) Hexil as a booster material is superior to TNT, but somewhat inferior to tetryl and TNA.

(2) It is extremely stable and is safer to handle than either tetryl or TNA, and makes a satisfactory booster.

(3) It can be manufactured by a simple process from sources which would not conflict with TNT manufacture, and because of the excellent yields obtained, and the cheapness of intermediates for it, its material cost should be less than for either tetryl or TNA.

(4) On account of the simplicity of the process, the installation of a plant for its manufacture would be less expensive than for an extension of the manufacturing facilities for either tetryl or TNA.

(5) On account of the simplicity of operating methods, labor costs would be less than for either of the other materials.

ACIDITY AND ACIDIMETRY OF SOILS.[1] I—STUDIES OF THE HOPKINS AND PETTIT METHOD FOR DETERMINING SOIL ACIDITY

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Received October 14, 1919

The Hopkins and Pettit method of determining soil acidity[2] proposed in 1902 is essentially as follows: 100 g. of soil are shaken in a bottle of 400 cc. capacity with 250 cc. of 5 per cent commercial common salt solution for 3 hrs. 125 cc. of the clear liquid are taken off, boiled to expel carbon dioxide, and titrated using phenolphthalein as an indicator. The results are multiplied by 3 as a factor to determine the total amount of base required. Later[3] a normal solution of potassium nitrate was substituted for the 5 per cent commercial common salt and the factor 2.5 recommended. The modified method is still the provisional method of the A. O. A. C. for determining the acidity of soils.

Veitch[4] criticizes the Hopkins method upon the grounds that it indicates only the apparent need for lime or the most urgent need, and claims further that the acidity shown by this method is largely due to aluminates. He also notes that there is a great discrepancy between the Hopkins method and that proposed by himself[5] upon soils high in organic matter. Harris[1] claims that the acidity shown by this method is due to selective ion absorption by the soil colloids, basing his views upon the fact that the acidity shown by the extract is dependent upon the character of the salts used. Freer[2] also holds this view. Truog[3] strenuously combats the theory of colloidal absorption and brings evidence to support the view of Hopkins that the reaction is one of double decomposition between the acids or acid salts in the soil and the neutral salt solution. Parker[4] concluded from analysis of extracts prepared by treating soils with potassium chloride and potassium acetate that the base was absorbed to a little greater extent than it was liberated by the soil and that the excess of the anion should be accounted for by the presence of the corresponding acid. Brogue[5] states that it has been repeatedly proven that the base liberated by the soil is usually not merely equivalent to the base absorbed from the solution. Sullivan,[6] Morse and Curry,[7] Abbott, Conn and Smalley,[8] Ruprecht,[9] and others have noted the presence of aluminum and iron in salt extracts from acid soils. Rice[10] concludes from hydrogen-ion concentration studies upon 31 soils using the indicator method of Sörensen[11] that when so-called acid soils are shaken with salt solutions part of the cation of the salt is absorbed and an equivalent quantity of the base from the soil is given up to the solution.

It was to test the above points that the following investigations were made.

EXPERIMENTAL

Harris obtained different lime requirements for soils by repeated shaking with different salt solutions. These experiments were repeated in this laboratory using yellow-gray silt loam, and similar differences were obtained as was reported by Harris for different salts. As Hopkins claims that the reaction between the neutral salt solution and the soil is one of equilibrium, the end reaction would be practically impossible to realize by such a treatment. To overcome the objections which would arise from the above method provisions were made for forcing the salt solutions through the soil, so that the soil particles would be continually bathed by fresh solutions.

Twenty grams of yellow-gray silt loam[12] were placed upon a dry filter paper and the salt solution was allowed to filter through. The filtrate was boiled and treated with 0.04 *N* potassium hydroxide at room temperature using phenolphthalein as an indicator, with the results shown in Table I.

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[1] From a thesis submitted to the faculty of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Acknowledgment is made of many helpful suggestions and criticisms from Prof. C. G. Hopkins and Prof. A. H. Noyes.

[2] Nineteenth Annual Proceedings, O. A. C., U. S. Dept. of Agr., Bureau of Chemistry, *Bulletin* **73** (1902), 114.

[3] U. S. Dept. of Agr., Bureau of Chemistry, *Bulletin* **107** (1908), 20; Hopkins, "Soil Fertility and Permanent Agriculture," **1910**, 566.

[4] *J. Am. Chem. Soc.*, **26** (1914), 637.

[5] *Ibid.*, **24** (1902), 1120.

[1] Michigan Agr. College and Station, *Bulletin* **19** (1914).

[2] Penn. Dept. Agr., *Bulletin* **261** (1915), 106.

[3] *J. Phys. Chem.*, **20** (1916), 157.

[4] THIS JOURNAL, **6** (1914), 831.

[5] *J. Phys. Chem.*, **19** (1915), 665.

[6] U. S. Geol. Survey, *Bulletin* **312** (1907).

[7] New Hampshire Agr. Station, *Report* **1906-08**, 271.

[8] Indiana Agr. Expt. Station, *Bulletin* **170** (1913).

[9] Mass. Agr. Expt. Station, *Bulletin* **161** (1915).

[10] *J. Phys. Chem.*, **20** (1916), 214.

[11] *Biochem. J.*, **21** (1909), 131; Walpole, *Biochem.*, **5** (1911), 207; **8** (1914), 628.

[12] Sample No. 1. Subsoil from Southern Illinois. Lime requirement Hopkins Method 4.2T., Veitch Method 5.6T., per acre of soil of 2,000,000 lbs.

Table I—Acidity of Different Fractions of Various Salt Solutions Filtered through an Acid Soil

Salt Used	Cc. 0.04 N KOH Required for 100 cc.	250 cc.	250 cc.	250 cc.	Total	Equivalent to T. $CaCO_3$
N KNO_3.....	36.40	2.8	1.2	0.5	40.5	4.05
N KCl......	35.95	4.3	2.1	0.5	39.95	3.99
N $NaNO_2$....	26.50	9.2	1.8	1.4	38.9	3.89
N NaCl......	31.20	6.4	1.4	...	39.0	3.90
N $CaCl_2$......	31.40	5.4	1.3	0.5	38.6	3.86

The greatest difference shown is 0.19 T., calculated as calcium carbonate, which may easily be accounted for by errors in reading the end-point. It will be noted that the acidity of the sodium nitrate extract was quite marked even after 600 cc. had filtered through, while the first 100 cc. showed the lowest acidity. That none of the extractions were carried to completion is evident, but all, with the possible exception of that with sodium nitrate, were carried to a point beyond which it was impossible to measure the acidity with any degree of accuracy by the ordinary indicator methods. The calcium salt extract would be expected to show a slower reaction after the first surface reaction because of the greater insolubility of calcium compounds which would be formed upon the surface of the soil grains.

INDICATOR EFFECTS—In the first two series of extracts, a precipitate which had a rather marked effect upon the indicator was always formed in considerable quantity. The pink color produced by the addition of a slight excess of base disappeared after a time even when the titrating flask was tightly stoppered. By the further addition of base the color could be brought back. The end-point is also markedly influenced by the amount of indicator present. It is quite apparent that the indicator is absorbed to a marked extent by the precipitate, and instead of the simple equilibrium

$$\underset{\text{colorless}}{\text{HIn}} \rightleftarrows \underset{\text{colored}}{\text{H}^+ + \text{In}^-}$$

there must be taken into consideration the equilibrium with the absorbed indicator

$$\underset{\text{absorbed}}{\text{HIn}} \rightleftarrows \underset{\text{colorless}}{\text{HIn}} \rightleftarrows \underset{\text{colored}}{\text{H}^+ + \text{In}^-}.$$

Two equal quantities of a potassium salt extract of an acid soil gave readings, as shown in Table II, which clearly indicate the variation in results which may be obtained by using different amounts of indicator.

Table II—Effect of Different Amounts of Indicator upon Titration End-Point

Phenolphthalein Used Drops	0.04 N KOH Required Cc.
4	62.7
10	61.1

In several instances a point was reached which showed no visible color change with four or five drops of indicator, while upon the addition of larger quantities a marked color change was observed. To overcome as far as possible the variation due to the indicator the same quantity was used in each case unless otherwise stated.

EFFECT OF TEMPERATURE UPON TITRATION—The temperature at which the titration is carried out was found to produce an effect which is shown in Table III. Two equal quantities of potassium nitrate extract were titrated with 0.04 N potassium hydroxide using the same quantity of phenolphthalein as an indicator. The only difference between the duplicates was that of temperature.

Table III—Effect of Temperature upon Titration End-Point

Temp. ° C.	Cc. KOH
22	16.7
85	19.2

EFFECT OF TEMPERATURE UPON THE AMOUNT OF ACIDITY SHOWN—If the Hopkins method is a measure of the colloidal adsorption for the base by a soil as maintained by Harris[1] there should be a temperature effect which could be measured. Travers[2] has shown that the adsorption of carbon dioxide by charcoal decreases markedly with rise in temperature, and we may expect a similar change to be shown by soils in contact with neutral salt solutions.

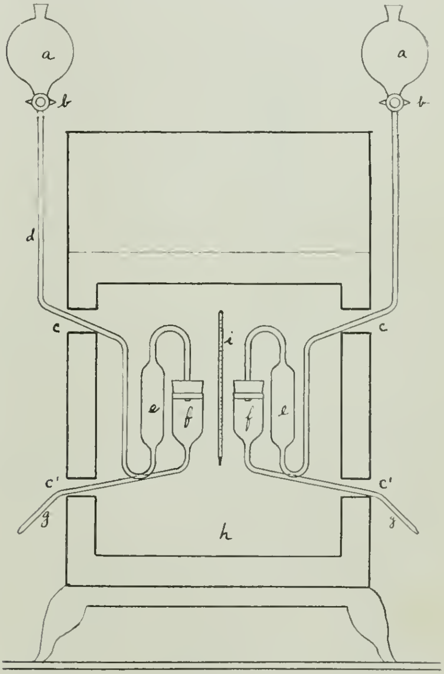

Fig. 1

To test this theory an apparatus, shown in Fig. 1, was arranged in a constant temperature electrical oven of the Freas type. The apparatus was arranged in duplicate. *a* is the receptacle for the neutral salt solution, *b* a stopcock for regulating the flow of the neutral salt through tube *d* which passes through the ventilating openings *c* provided by the manufacturers in the stock oven. The bulb *e* serves to bring the salt solution to the temperature of the oven before it runs into the receptacle *f* which contains the soil under investigation. The filtrate passes out of the apparatus through tube *g*, through ventilating openings in the oven at *c'*, and is caught in measuring flasks;

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[1] *Loc. cit.*

[2] *Proc Roy. Soc. London,* **74** (1904), 126.

i is a thermometer placed in the center of the oven for noting the temperature.

Twenty grams of soil were placed in the receptacle, normal potassium nitrate solution allowed to percolate through, and titrated at room temperature with results as shown in Table IV.

TABLE IV—EFFECT OF TEMPERATURE UPON REACTION BETWEEN ACID SOIL AND NEUTRAL SALT SOLUTION

	Temperature			
	90° ± 1°		25° ± 1°	
Percolate Cc.	0.04 N KOH Cc.	$CaCO_3$ T.	0.04 N KOH Cc.	$CaCO_3$ T.
100	37.85	3.785	36.4	3.64
400	3.15	0.315	3.0	0.30
Total 500	41.00	4.1	39.4	3.94

The temperature effect is very slight, and certainly does not indicate colloidal adsorption, unless this may be an exceptional case.

EFFECT OF STRENGTH OF SALT SOLUTION—Potassium nitrate solutions of different strengths were filtered through 20 g. samples of yellow-gray silt loam and the filtrate titrated with 0.04 N KOH, using phenolphthalein as an indicator with results shown in Table V.

TABLE V—EFFECT OF STRENGTH OF SALT SOLUTION UPON THE TOTAL AMOUNT OF ACIDITY

Fractions Cc.	Cc. 0.04 N KOH Required		
	N KNO_3	0.5 N KNO_3	0.1 N KNO_3
1—100	35.0	33.3	18.3
2—100	3.5	4.7	7.6
3—100	1.2	1.5	4.3
4—100	0.8	0.9	3.7
5—100	0.5	0.6	3.3
6—100	..	..	1.6
Total.. ..	40.8	41.0	38.8
as T. $CaCO_3$	4.08	4.10	3.88

It will be noted that with the stronger salt solutions the greatest acidity is shown in the first 100 cc. but rapidly falls while the weaker solutions show a higher acidity in succeeding fractions. Evidently end extractions would lead to the same end results regardless of the strength of the salt solution.

Further study of this reaction was made by extracting 10 g. samples of the same soil with various strengths of potassium nitrate solution and titrating the acid in the first 100 cc. of the percolate. The results are tabulated in Table VI.

TABLE VI—ACIDITY SHOWN IN FIRST 100 CC. FILTRATE FROM ACID SOIL, USING NEUTRAL SALT SOLUTIONS OF VARIOUS STRENGTHS

Normality of KNO_3	0.04 N KOH Required Cc.	Calculated as T. $CaCO_3$
1.00	15.2	3.40
0.50	15.3	3.06
0.25	15.2	3.04
0.125	13.25	2.65
0.0625	8.00	1.60
0.0312	4.10	0.82
0.0156	1.95	0.39
0.0078	1.17	0.23

The acidity of the first portion of the extract increases with increase in concentration of the neutral salt solution.

TABLE VII—AMOUNTS OF LIME ABSORBED BY ACID SOIL FROM SOLUTIONS OF VARIOUS STRENGTH

Lime Added Calculated as T. $CaCO_3$	Absorbed by Soil T. $CaCO_3$	Left in Solution T. $CaCO_3$	Final Normality of Solution
12	11.71	0.29	0.000285
14	13.56	0.64	0.00064
16	14.59	1.41	0.0014
20	16.75	3.25	0.0032
30	20.93	9.07	0.009
40	24.96	15.04	0.015

EXAMPLES OF SO-CALLED COLLOIDAL ABSORPTION

As examples of what are usually considered colloidal phenomena the following experiments are submitted.

EXPERIMENT I—20 g. of yellow-gray silt loam were shaken with various amounts of lime contained in 200 cc. of solution for 12 hrs. and aliquot parts of the clear liquid were titrated with results as shown in Table VII.

A greater portion of the lime is absorbed from the dilute solutions than from the more concentrated, thus apparently following the colloidal absorption law.

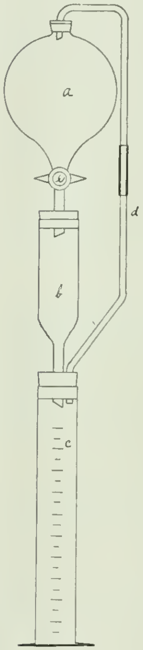

FIG. 2

EXPERIMENT II—20 g. of soil were placed in an extracting apparatus (*b*, Fig. 2), and a 0.04 N calcium hydroxide solution allowed to percolate through. In the diagram *a* is the receptacle for the base, *e* a stopcock for regulating the flow of the base into *b*, and *c* a graduated receiver connected with tube *d* which serves to equalize the pressure. The apparatus is a closed system and duplicate results were easily obtained. 237.2 cc. of filtrate[1] passed through before a pink color could be detected, with phenolphthalein as an indicator, representing a lime adsorption at this point of 23.7 T. as calcium carbonate. At the close of the experiment 537.6 cc. of filtrate had percolated through, the last 50 cc. being 0.0285 N base, while the soil had absorbed a total of 35.28 T. of lime as calcium carbonate. 15.82 T. of lime were washed out by the first 700 cc. of distilled water, the end fraction passing through 0.00242 N alkali. 19.46 tons of lime were still left in the soil.

The details are given in Table VIII, in which A and B are duplicate determinations.

TABLE VIII—AMOUNT OF LIME ABSORBED BY ACID SOIL FROM SOLUTION OF CONSTANT STRENGTH PERCOLATING THROUGH THE SOIL

	A		
	$Ca(OH)_2$		
Percolate Cc.	Calculated as T. $CaCO_3$ Absorbed	Per cent Absorbed	Calculated as T. $CaCO_3$ in Percolate
236.5	23.65	100.0	0.00
27.0	2.50	92.6	0.20
28.5	1.95	68.4	0.90
45.0	1.97	43.7	2.53
51.4	1.61	31.3	3.53
48.6	0.93	19.1	3.93
50.0	1.04	20.8	3.96
50.5	1.45	28.7	3.60
Total 537.5	35.10		
	B		
238.0	23.80	100.0	0.00
43.2	4.17	96.6	0.15
58.0	3.04	52.2	2.76
50.5	1.24	24.5	3.81
50.0	1.08	20.2	3.92
50.0	1.15	23.0	3.85
50.0	0.99	19.8	4.01
Total 539.7	35.47		

At the completion of the experiment water was added and the first 700 cc. carried through the equivalent of 16 tons of lime as $CaCO_3$, or nearly half the amount absorbed.

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[1] Figures given are average of results **A** and **B** below.

EXPERIMENT III—Twenty gram samples of yellow-gray silt loam were shaken for 3 hrs. with 200 cc. of 0.04 *N* calcium hydroxide and potassium hydroxide, respectively. Since the solution containing the potassium hydroxide would not settle, 25 cc. of normal potassium nitrate were added to both the calcium and potassium hydroxide solutions, and filtered. Titrations of 100 cc. of filtrate with 0.04 *N* hydrochloric acid gave the results included in Table IX.

TABLE IX—AMOUNT OF BASE NOT ABSORBED BY AN ACID SOIL FROM SOLUTIONS OF EQUIVALENT STRENGTH

BASE USED	0.04 *N* HCl Required to Neutralize Filtrate Cc.
$Ca(OH)_2$	7.7
KOH	31.9

As the potassium hydroxide solution was neutralized, a copious precipitate of aluminum hydroxide was formed. No precipitate was noted upon neutralizing the calcium hydroxide solution.

It would appear from this experiment that the soil has a greater absorption power for calcium than for potassium, which is not indicated by other experiments. A chemical difference in the action of the two bases seems the more simple explanation. Potassium aluminate is soluble while calcium aluminate is not. Both are unstable except in the presence of a base. Since the potassium aluminate passes into solution it is titrated above while the calcium aluminate is precipitated around the soil particles.

This apparently throws doubt upon the magnitude of the colloidal adsorption effects which may be assumed from Expts. I and II above. The probable cause would seem to be precipitation effects. Hydrolysis will account for the rapid washing out of the lime when water is added in Expt. II.

EXCHANGE OF BASE

There is considerable doubt whether, when an acid soil is shaken up with a neutral salt, there is a complete exchange of base. Rice[1] comes to the conclusion that there is an equivalent exchange and that the acidity is due to the aluminum salts. He further claims that the ordinary methods of analysis are too crude to determine this accurately. Sharp and Hoagland[2] by use of the hydrogen electrode show that soil acidity is due to an excess of hydrogen ions, and that the acidity is increased by the presence of certain neutral salts.

Analysis was made of the potassium nitrate extract of yellow-gray silt loam with results shown in Table X.

TABLE X—ANALYSIS OF POTASSIUM NITRATE EXTRACT OF AN ACID SOIL

	627 Cc. of 0.04 *N* Acid = Gram
SiO_2	0.04741
P_2O_5	0.00576
Al_2O_3	0.38822
Fe_2O_3	Trace
CaO	0.06025
Mn_3O_4	0.04839
MgO	0.19901

The acid combined with the alumina would be equivalent to 570 cc. of 0.04 *N* acid leaving an excess of 57 cc. to be accounted for in other ways.

Since, as has been shown by Blum,[1] alumina is completely precipitated before the hydrogen-ion concentration drops to a value of 10^{-7} and, conversely, alumina will not pass into solution until the hydrogen-ion concentration reaches a value higher than 10^{-7}, it is reasonable to conclude that there must be some absorption of base before the alumina will pass into solution. If this is true we must assume that the dissolution of alumina is a secondary reaction, and the above analysis certainly points in this direction.

It was noted that strongly acid extracts of this soil were highly colored with iron. To test the question of why iron is not also taken out in larger quantities by a similar secondary reaction, 100 g. samples of yellow-gray silt loam were shaken with 250 cc. of 0.04 *N* acids and a partial analysis made of 125 cc. of the filtered extracts. The results are given in Table XI.

TABLE XI—PARTIAL ANALYSIS OF WEAKLY ACID EXTRACTS OF AN ACID SOIL

ACID USED	Al_2O_3 Gram	Fe_2O_3
Acetic	0.00383	Trace
Nitric	0.06913	Trace
Hydrochloric	0.07049	Trace

The solutions were still acid and upon neutralization white precipitates of aluminum hydroxide were formed in the hydrochloric and nitric acid extracts but none was noted in the acetic acid extract until it was neutralized and boiled. It would seem that when dilute acids are allowed to act upon an acid soil alumina is first brought into solution, and that neutral salts, when brought into contact with an acid soil, show the properties of a weak acid in this respect.

DIALYSIS

Normal potassium nitrate solution was shaken with yellow-gray silt loam and allowed to settle. The supernatant liquid was drawn off into a collodion bottle and subjected to dialysis with the results given in Table XII.

TABLE XII—DIALYSIS OF A NEUTRAL SALT IN CONTACT WITH AN ACID SOIL

	0.04 *N* KOH to Neutralize Cc.
1st water fraction	35.1
2nd water fraction	12.06
3rd water fraction	24.9
Left in flask	24.9
TOTAL	96.96

74 per cent of the titratable acid had passed through the membrane. As the liquid left in the dialyzing flask was being titrated a heavy precipitate formed, while that which passed through remained clear upon neutralization. It was evident that the acid passed through while the aluminum hydroxide did not. This, however, was to be expected, as this is one of the recognized methods for the preparation of colloidal aluminum hydroxide.[2]

DISTILLATION OF SOIL EXTRACT

Attempts were made to remove acid from potassium nitrate and chloride extracts of soil by prolonged distillation with steam but without success. Better success followed the distillation of the potassium acetate extract of the yellow-gray silt loam as shown in Table XIII.

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[1] *Loc. cit.*

[2] *J. Agr. Res.*, [3] 7 (1916), 124.

[1] *J. Am. Chem. Soc.*, 7 (1916), 1282.

[2] Graham, *Ann.*, 121 (1866), 41.

TABLE XIII—DISTILLATION OF A POTASSIUM ACETATE EXTRACT OF AN ACID SOIL, AND OF STOCK SOLUTION OF POTASSIUM ACETATE
(*Acidity in Terms of 0.04 N Base*)

Potassium Acetate Extract		Potassium Acetate Stock Solution	
Distillate	Residue	Distillate	Residue
72.9 Cc.	21.9 Cc.	8.6 Cc.	1.95 Cc.

Phenolphthalein was used as an indicator. This experiment shows the presence of appreciable quantities of acetic acid in the soil extract. About three-fourths of the acid shown by the extract was distilled over.

Walter Crum[1] prepared colloidal aluminum hydroxide by separating the acetic acid by heating, but as there were only traces of aluminum salts carried by the potassium acetate extract[2] it can hardly be conceived that the phenomena may be accounted for by the presence of these salts, but rather that there is an excess of acid.

COMPARISON OF CATION AND ANION ABSORPTION

To compare the cation and anion absorption of the yellow-gray silt loam from neutral salt solution a 0.0358 *N* solution of calcium chloride was allowed to percolate through 20 g. of the soil in the apparatus shown in Fig. 2. The extract was analyzed for calcium and chlorine. The calcium was determined in an aliquot portion of the extract which had been freed from iron and aluminum by first precipitating as the oxalate and titrating the precipitate with a standard potassium permanganate in the presence of dilute sulfuric acid. The chlorine was determined by the Volhard method[3] using 0.04 *N* solutions. The results are tabulated in Table XIV.

TABLE XIV—ANALYSIS OF FRACTIONS OF EXTRACT OF AN ACID SOIL BY A NEUTRAL SALT SOLUTION TO DETERMINE CATION AND ANION ABSORPTION

Extract Fractions Cc.	Calcium Normality	Chlorine Normality	Acid Normality
1—50	0.0180	0.0348	0.0046
2—50	0.0314	0.0358	0.0037
3—50	0.0332	0.0358	0.0028
4—50	0.0335	0.0358	0.0022

The cation is absorbed to a measurable extent, for which the change in acidity fails to account. There must, therefore, have been an exchange of base. This confirms the fact that there is a basic exchange regardless of the neutral salt used. (See analysis of potassium nitrate extract.) The anion is absorbed little or not at all. The slight absorption shown in the first 50 cc. of extract is probably due to the wetting of the particles and to a slight dilution of the extract by moisture in the air-dried soil. A small amount of precipitate was formed in each case upon neutralizing the extract.

SUMMARY

1—When normal solutions of potassium nitrate, potassium chloride, sodium nitrate, sodium chloride, and calcium chloride were percolated through an acid soil all gave the same end titrations, using phenolphthalein as an indicator. This corroborates Hopkins' statements.

2—The acidity of the salt extract of an acid soil is independent of the temperature within the range from 25° to 90° C.

3—The precipitate formed in titrating the soil extract obtained by the Hopkins method absorbs the indicator to a marked extent. The end result depends upon the temperature, time, and amount of indicator used.

4—The acidity of the first portions of the neutral salt extracts of an acid soil increases with increase in concentration of the neutral salts.

5—The difference in absorption of calcium and potassium from solutions of their bases by an acid soil may be accounted for by precipitation effects.

6—There is a marked basic exchange when a neutral salt solution is added to an acid soil, by which alumina is carried into solution. This, however, does not account for the total acidity of the solution.

7—When acid soil is extracted with potassium acetate solution, a portion of acetic acid may be distilled off from the extract, showing the presence of free acid.

8—Exchange of acid radicals when an acid soil is treated with a neutral salt solution was not noted.

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[1] *Ann.*, **89** (1854), 168.

[2] Compare Conner, THIS JOURNAL, **8** (1916), 35.

[3] *Ann.*, **190**, 1.

THE USE OF CUPFERRON IN QUANTITATIVE ANALYSIS[1]

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Received September 8, 1919

INTRODUCTION

The increasing use of cupferron (the ammonium salt of nitrosophenylhydroxylamine, $C_6H_5.N.NO.ONH_4$) for the determination of zirconium in its ores and metallurgical products, as well as for minor purposes such as the separation of iron and titanium from manganese and aluminum in limestone analysis,[2] and other determinations for which it has been recommended, makes a review of the possibilities and limitations of this reagent highly desirable. This paper presents a review of the literature dealing with the use of cupferron as a quantitative precipitant, and gives the results of many tests which were performed at this Bureau in connection with an attempt to adapt the cupferron method to the determination of zirconium in its ores and metallurgical products.

GENERAL PRINCIPLES

Cupferron precipitates are salts in which the ammonium radical of the reagent has been replaced by metals. Precipitations are performed in cold solutions containing free mineral or organic acids. Cold solutions must be employed to prevent decomposition of the reagent into various organic substances, such as nitrobenzene, and the temperature of precipitation is usually specified as "cooled in ice water." A 6 per cent water solution of the reagent is used and complete precipitation is indicated by the formation of a temporary flash of a fine, white precipitate which redissolves, as contrasted with the flocculent insoluble cupferron precipitates. Precipitation is usually immediate and filtration is carried on through paper and cone by means of gentle suction. The wash waters are always cold and range from 5 per cent (by volume) ammonium hydroxide for iron precipitates to 10 per cent (by volume) hydrochloric acid for titanium and zirconium precipitates. Ignitions of cupferron precipitates are carried on very carefully in the early stages owing to excessive liquefaction when wet precipitates are ignited, and to the heavy liberation of gaseous products from dried precipitates. The ordinary procedure calls for ignition to oxides, although some variations will be noted in certain methods reviewed below.

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[1] Published by permission of the Director of the Bureau of Standards.

[2] Private communication from J. A. Holladay, Electro-Metallurgical Co., Niagara Falls, N. Y.

HISTORICAL

The use of cupferron as a quantitative reagent was recommended originally by Baudisch[1] who showed its application to the determination of iron in brown iron ore and of iron and copper in nickel ore. He also described the properties and behavior of the reagent, and enumerated instances where it could be used to advantage. Its uses have since been studied by many investigators and it has been proposed as a quantitative precipitant under varying conditions (often loosely defined in the earlier papers) for copper, iron, titanium, zirconium, thorium, and vanadium. For convenience, the work done on each of these determinations will be given below under separate headings.

Tables of results will not be given unless authors have given definite conditions for precipitation.

QUANTITATIVE DETERMINATIONS WITH CUPFERRON

COPPER

(1) HISTORICAL—Biltz and Hödtke[2] found that complete precipitation of copper takes place in weak solutions of hydrochloric acid and in solutions of acetic acid containing sodium acetate, but not in the presence of excessive amounts of mineral acids. They washed the precipitate first with water, then with 1 per cent sodium carbonate solution to remove excess reagent, finally with water, and then ignited to oxide. Their data demonstrated a very great accuracy for the method.

Hanus and Arn. Soukup[3] experienced considerable difficulty in precipitating copper from dilute sulfuric acid solutions but obtained good results when filtration on a gooch immediately followed precipitation. The precipitate was washed with cold water, dried, ignited to oxide, and reduced with methyl alcohol.

Baudisch[4] in a second paper dealt with the properties of cupferron and gave a method for its preparation.

Fresenius[5] demonstrated that copper can be quantitatively precipitated from acetic acid solution containing ammonium acetate. The precipitate was washed with 1 per cent sodium carbonate solution, dried, ashed, ignited with sulfur in a Rose crucible in an atmosphere of hydrogen, and weighed as cuprous sulfide.

Weber[1] dealt mainly with the technique of the use of cupferron and cited the work of Biltz and Hödtke and of Nissenson.[2]

Baudisch and King[3] reviewed the desirable features of the cupferron method, calling attention to the fact that copper can be quantitatively determined in mineral or acetic acids, and giving directions for the preparation of cupferron.

(2) FAVORABLE PROCEDURE FOR PRECIPITATION—For the determination of copper, high mineral acidity is objectionable, but weak solutions of hydrochloric or sulfuric acids are permissible, while acetic acid in sodium or ammonium acetate solutions gives the best results. Cold water is the most satisfactory washing medium. The ignition is usually carried to oxide, although some authors prefer to transform the oxide to cuprous sulfide or metallic copper.

(3) SEPARATIONS WHICH HAVE BEEN ATTEMPTED. (*a*) *Copper from Zinc*—Biltz and Hödtke demonstrated that a very satisfactory separation of copper from zinc could be accomplished in acetic acid solution. Hanus and Soukup tried the separation in weak sulfuric acid solution and obtained results which were not as satisfactory as those of Biltz and Hödtke.

(*b*) *Copper from Cadmium*—Biltz and Hödtke obtained good separation in weak hydrochloric acid but not in acetic acid. Hanus and Soukup performed the separation in weak sulfuric acid solution.

(*c*) *Copper from Iron*—Biltz and Hödtke found that a good separation could be secured if the copper-iron cupferron precipitate obtained in weak acid solutions was washed with ammonium hydroxide, which dissolved the copper precipitate and not the iron compound.

Fresenius obtained an excellent separation by precipitation in acetic acid solution containing ammonium acetate followed by washing with ammonium hydroxide.

(4) INTERFERING SUBSTANCES—Biltz and Hödtke pointed out that lead, silver, mercury, and tin interfere. Fresenius added bismuth to the list.

To the above list should be added iron, titanium, zirconium, cerium, thorium, tungsten, vanadium, and undoubtedly several other elements.

The interference of iron, titanium, zirconium, cerium, and thorium, and possibly lead, mercury, tin, and bismuth can be avoided by treating the cupferron precipitate with ammonia and reprecipitating the dissolved copper by the addition of weak acid.

(5) SUMMARY—The use of cupferron for the determination of copper is of classical interest and not of any practical importance.

IRON

(1) HISTORICAL—Baudisch[4] pointed out that iron was precipitated by cupferron as reddish brown flocks, soluble in ether and in acetone.

Biltz and Hödtke[5] showed that iron could be precipitated with copper and quantitatively separated from it by the use of an ammonium hydroxide wash. Fresenius[1] used Biltz and Hödtke's method with good results in hydrochloric, sulfuric, and acetic acid solutions. He cited practical tests of the method with excellent results in the analysis of a manganese ore and the analysis of a ferromanganese.

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[1] *Chem.-Ztg.*, **33** (1909), 1298.
[2] *Z. anorg. Chem.*, **66** (1910), 426
[3] *Ibid.*, **68** (1910), 52.
[4] *Chem.-Ztg.*, **35** (1911), 913.
[5] *Z. anal. Chem.*, **50** (1911), 35.

[1] *Z. anal. Chem.*, **50** (1911), 50.
[2] *Z. angew. Chem.*, **23** (1911), 969.
[3] THIS JOURNAL, **3** (1911), 629.
[4] *Chem.-Ztg.*, **33** (1909), 1298.
[5] *Loc. cit.*

Nissenson[1] used the reagent for the separation of iron from nickel and cobalt in speiss.

Ferrari[2] published a paper on the rapid determination of iron in the presence of soluble organic substances. He showed that quantitative determinations of iron in this class of material can be carried out in 1.5 hrs. by direct precipitation with cupferron of the chlorine-treated hydrochloric acid solutions of the organic material, followed by filtration of the precipitate and ignition to Fe_2O_3. He stated that such elements as copper, silver, lead, mercury, tin, bismuth, titanium, and zirconium interfere with the determination.

(2) FAVORABLE PROCEDURE FOR PRECIPITATION—Iron can be precipitated from dilute solutions of the mineral acids, hydrochloric, sulfuric, and nitric, and from acetic acid. Complete precipitation has been obtained at this Bureau in solutions containing 20 per cent by volume of sulfuric acid. The precipitate may be washed with cold 2 *N* hydrochloric acid, ammonium hydroxide, or water. Ignition is carried to the oxide.

(3) SEPARATIONS WHICH HAVE BEEN ATTEMPTED. (*a*) *Iron from Copper*—Biltz and Hödtke obtained perfect separations from copper. See COPPER 3*c*.

Fresenius demonstrated the exactness of this method. See COPPER 3*c*.

(*b*) *Iron from Manganese*—Fresenius carried out perfect separations of these elements in hydrochloric acid solution.

(*c*) *Iron from Zinc*—Fresenius showed that complete separation can be had in dilute sulfuric acid solution.

(*d*) *Iron from Aluminum and Chromium*—Biltz and Hödtke performed this separation in mineral acid solution, and washed the precipitate with 2 *N* hydrochloric acid, water, ammonium hydroxide, and finally water. Fresenius showed that the separation of iron from aluminum and chromium is complete in dilute hydrochloric acid solution.

(*e*) *Iron from Nickel and Cobalt*—Baudisch showed that this separation was satisfactory in hydrochloric acid solution. Biltz and Hödtke also obtained a good separation in mineral acids. Fresenius performed perfect separations of iron from nickel and cobalt in dilute sulfuric acid solution.

(*f*) *Iron from the Alkalies and Alkaline Earths*—Fresenius showed that no trouble was experienced in carrying out these separations in appropriate dilute mineral acids.

(*g*) *Iron from Phosphorus*—Fresenius also demonstrated the fact that iron can be completely separated from phosphorus in dilute hydrochloric acid solutions.

(4) INTERFERING SUBSTANCES—Copper, lead, silver, mercury, tin, and bismuth interfere. This, however, is not serious, since their prior separation by means of hydrogen sulfide is an easy matter.

Titanium, zirconium, cerium, thorium. tungsten, vanadium, and undoubtedly several other elements of this analytical group also interfere.

(5) SUMMARY—The determination of iron by the cupferron method does not offer any advantages over ordinary established procedures. This reaction may, however, be of value in certain group separations such as the separation of iron and titanium from aluminum and manganese in limestone analysis as proposed and used by Mr. Holladay.[1]

TITANIUM

(1) HISTORICAL—Schroeder[2] found that titanium could be quantitatively precipitated from acid solutions. Bellucci and Grassi[3] showed that cupferron quantitatively precipitated the yellow compound $(NO.NC_6H_5O)_4Ti$, which they ignited to TiO_2.

Thornton[4] demonstrated that this method was one of high accuracy in a solution containing varying amounts of sulfuric acid and tartaric acid as is shown by Table I.

TABLE I

EXPT. No.	TiO_2 Used G.	TiO_2 Found G.	Error G.	H_2SO_4 1 : 1 Cc.	Tartaric Acid Used G.	Vol. of Solution Cc.
9	0.1428	0.1429	+0.0001	5	0.5	200
10	0.1066	0.1069	+0.0003	20	1.5	400
11	0.1064	0.1067	+0.0003	30	2.0	400
12	0.1064	0.1066	+0.0002	40	2.0	400

In Table II will be found the tabulation of results obtained in tests along the same line carried on at this Bureau. These show that complete precipitation can be made in solutions containing 40 per cent by volume of concentrated sulfuric acid.

TABLE II

EXPT. No.	TiO_2 Used G.	TiO_2 Found G.	Error G.	H_2SO_4 Per cent by Vol.	Vol. of Solution Cc.
1	0.0999	0.0997	—0.0002	5	400
2	0.0999	0.1000	+0.0001	10	400
3	0.0999	0.0999	0.0000	15	400
4	0.0999	0.1001	+0.0002	20	400
5	0.0999	0.1002	+0.0003	40	400

Qualitative tests of the above filtrates showed no titanium.

Brown[5] applied Thornton and Hayden's method to the analysis of titanium and zirconium in baddeleyite and zircon with good results.

(2) FAVORABLE PROCEDURE FOR PRECIPITATION—Titanium can be quantitatively precipitated from solutions containing as much as 40 per cent sulfuric acid by volume. The presence of tartaric acid causes no trouble. Presumably titanium can also be precipitated from solutions containing considerable hydrochloric, acetic, or tartaric acids. Nitric acid in high concentrations is not permissible on account of its action on the reagent.

(3) SEPARATIONS WHICH HAVE BEEN ATTEMPTED. (*a*) *Titanium from Aluminum*—Bellucci and Grassi

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[1] *Loc. cit.*

[2] *Ann. chim. applicata*, **4** (1915), 341.

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[1] *Loc. cit.*

[2] *Z. anorg. Chem.*, **72** (1911), 89.

[3] *Atti accad. Lincei*, [V] **22** (1913), 30.

[4] *Am. J. Sci.*, **37** (1914), 173, 407.

[5] *J. Am. Chem. Soc.*, **39** (1917), 2358.

showed that the separation of titanium from aluminum is quantitative. This observation was confirmed by Thornton who found, however, as shown in Table III, that the separation is sharp only in highly acid solutions, and that addition of tartaric acid is desirable.

TABLE III

Expt. No.	TiO_2 Used G.	Al_2O_3 Used G.	TiO_2 Found G.	Error G.	H_2SO_4 1 : 1 Cc.	Tartaric Acid Used G.	Vol of Solution Cc.
1	0.1066	0.1127	0.1179	+0.0113	5	...	200
2	0.1066	0.1127	0.1094	+0.0028	10	...	200
3	0.05715	0.1127	0.0590	+0.0018	5	1.2	200
4	0.0572	0.1127	0.0577	+0.0005	10	1.2	200
5	0.0575	0.1127	0.0579	+0.0004	15	1.2	200
6	0.0573	0.1127	0.0575	+0.0002	20	1.2	200
7	0.1067	0.1127	0.1072	+0.0005	20	1.5	400
8	0.1068	0.1127	0.1070	+0.0002	20	1.5	400

(*b*) *Titanium from Iron*—Thornton accomplished this separation by treating an acid tartaric acid solution of the two with hydrogen sulfide, adding ammonium hydroxide after the iron was reduced, continuing the addition of hydrogen sulfide and finally filtering off the iron sulfide. The titanium was then determined in the acidified filtrate. Data are given in Table IV.

TABLE IV

Expt. No.	TiO_2 Used G.	Fe_2O_3 Used G.	TiO_2 Found G.	Error Mg.
4	0.1428	0.2267	0.1424	—0.4
5	0.1428	0.2267	0.1430	+0.2
6	0.1066	0.2267	0.1068	+0.2
7	0.1063	0.2267	0.1061	—0.2

(*c*) *Titanium from Phosphorus*—Thornton demonstrated that phosphoric acid was without serious effect in strongly acidified solutions, as shown in Table V.

TABLE V

Expt. No.	TiO_2 Used G.	P_2O_5 Used G.	TiO_2 Found G.	Error G.	H_2SO_4 1 : 1 Cc.	Tartaric Acid Used G.	Vol. of Solution Cc.
13	0.1064	0.0711	0.1071	+0.0007	20	1.5	400
14	0.1066	0.0710	0.1067	+0.0001	25	1.5	400

Experiments carried on at this Bureau dealing with the effect of phosphoric acid in cupferron precipitations of titanium and zirconium are given in Table VI.

TABLE VI

$ZrO_2.TiO_2$ (1 : 1) Taken G.	H_2SO_4 Per cent by Vol.	Tartaric Acid G.	P_2O_5 Used G.	Weight of Ignited Oxide, G.	Error G.	Vol. Solution Cc.
0.2119	10	1.0	0.02	0.2126	+0.0007	400
0.2119	10	1.0	0.05	0.2129	+0.0010	400
0.2119	10	1.0	None	0.2117	—0.0002	400
0.2119	10	1.0	None	0.2122	+0.0003	400

The results show a contamination greater than that obtained by Thornton and this is directly attributable to zirconium, which forms more insoluble phosphates.

(*d*) *Titanium from Iron, Aluminum, and Phosphorus*—Thornton separated iron, first, by precipitating the reduced iron by ammonium sulfide in ammonium tartrate solution as outlined in *b*, and then proceeding as indicated in Table III. The accuracy of the method is shown in Table VII.

TABLE VII

Expt. No.	TiO_2 Used G.	Fe_2O_3 Used G.	Al_2O_3 Used G.	P_2O_5 Used G.	TiO_2 Found G.	Error G.	H_2SO_4 1 : 1 Cc.	Tartaric Acid G.	Vol. of Solution Cc.
15	0.1065	0.2036	0.1127	0.0154	0.1070	+0.0005	30	2	400
16	0.1066	0.2036	0.1127	0.0151	0.1068	+0.0002	30	2	400
17	0.1065	0.1018	0.1127	0.0153	0.1067	+0.0002	40	2	400
18	0.1067	0.1018	0.1127	0.0153	0.1069	+0.0002	40	2	400
19	0.1066	0.2267	0.2254	0.0153	0.1069	+0.0003	40	2.5	400
20	0.1066	0.2267	0.2254	0.0153	0.1073	+0.0007	40	2.5	400

(*e*) *Titanium from Platinum*—Since platinum is often introduced into titanium solutions by fusion operations, Thornton analyzed some solutions to which chlorplatinic acid had been added. The data, given in Table VIII, demonstrate that platinum introduced into solutions by fusion operations is without effect.

TABLE VIII

Expt. No.	TiO_2 Used G.	Pt Used (approx.) G.	TiO_2 Found G.	Error G.	H_2SO_4 1 : 1 Cc.	Vol. of Solution Cc.
21	0.1067	0.01	0.1071	+0.0004	40	400
22	0.1067	0.01	0.1066	—0.0001	40	400

(*f*) *Titanium from Boric Acid*—Since borax was used at this Bureau for the fusion of several ores, tests were carried out which showed that boric acid was without interfering action. The data obtained are given in Table IX.

TABLE IX

Expt. No.	$ZrO_2.TiO_2$ 1 : 1 G.	H_3BO_3 Taken G.	Tartaric Acid G.	$ZrO_2.TiO_2$ Found G.	Error G.	H_2SO_4 1 : 1 Cc.	Vol. of Solution Cc.
1	0.2104	0.5	1	0.2106[1]	+0.0002	40	400
2	0.2104	0.5	1	0.2103[1]	—0.0001	40	400

[1] Cupferron filtrate contained neither zirconium nor titanium

(*g*) *Titanium from Alkali Salts*—Tests made at this Bureau dealing with the effect of alkali salts confirmed the observation of Thornton and Hayden[1] concerning their effect in zirconium precipitations, namely, that the presence of excessive alkali causes high values and the obvious remedy when they are present is to carry out a preliminary precipitation with ammonium hydroxide, followed by solution of the precipitate in acid and precipitation by cupferron.

(*h*) *Titanium from Silica*—Experiments performed at this Bureau are listed in Table X, which shows that the separation of titanium (and zirconium) from silica is not complete. This is not a source of trouble, for silica in the final ignited precipitate can be volatilized with hydrofluoric acid with no loss of titanium (or zirconium) provided sufficient sulfuric acid is present.

TABLE X

Expt. No.	Approx. Amount of Soluble Silica in Solution when Treated with Cupferron G.	Weight Ignited Cupferron Ppt. ZrO_2-TiO_2-SiO_2 G.	Weight of SiO_2 in Precipitate G.
1	0.05	0.1651	0.0036
2	0.05	0.1978	0.0013
3	0.05	0.2107	0.0006

(*i*) *Titanium from Vanadium*—Tests performed at this Bureau demonstrated that it is not possible to separate titanium (and zirconium) from vanadium in either the quadrivalent or quinquivalent state. It will be noted that the separation is more nearly complete when vanadium is in the quadrivalent state, and it may be safely stated that contamination varies inversely as the acidity. Table XI gives the data obtained.

TABLE XI

Expt. No.	$ZrO_2.TiO$ Taken G.	H_2SO_4 Per cent by Volume	Tartaric Acid G.	V_2O_5 Taken G.	V_2O_4 Taken G.	Vol. of Solution Cc.	Weight of Cupferron Ppt. G.	Error G.
1	0.2120	10	1	None	None	400	0.2117	—0.0003
2	0.2120	10	1	None	None	400	0.2122	+0.0002
3	0.2120	10	1	None	0.02	400	0.2130	+0.0010
4	0.2120	10	1	None	0.05	400	0.2161	+0.0041
5	0.2120	10	1	0.02	None	400	0.2270	+0.0150
6	0.2120	10	1	0.05	None	400	0.2489	+0.0369

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[1] *Am. J. Sci.*, **38** (1914), 137.

The presence of vanadium in both the cupferron precipitates and in the cupferron filtrates was qualitatively established in Expts. 3, 4, 5, and 6. The use of ammonium hydroxide wash solution does not lessen the contamination.

(*j*) *Titanium from Uranium*—Since it was considered likely that some zirconium steels might contain uranium, tests were made at this Bureau to establish the effect of uranium in the cupferron precipitation. The data given in Table XII demonstrate that uranium does not interfere when in the sexivalent state, but does interfere in the quadrivalent state.

TABLE XII

EXPT. No.	$ZrO_2.TiO_2$ Taken G.	H_2SO_4 Per cent by Volume	Tartaric Acid G.	UO_3 Taken G.	UO_2 Taken G.	Vol. of Solution Cc.	Weight Cupferron Ppt. G.	Error G.
1	0.2114	10	1	None	None	400	0.2114	0.0000
2	0.2114	10	1	None	0 02	400	0.2122	+0.0008
3	0.2114	10	1	None	0.05	400	0.2179	+0.0065
4	0.2114	10	1	0.02	None	400	0 2118	+0.0004
5	0.2114	10	1	0.05	None	400	0.2116	+0.0002

Qualitative tests showed the presence of uranium in both precipitates and filtrates in Expts. 2 and 3 and no uranium in the precipitates in Expts. 4 and 5.

(*k*) *Titanium from Tungsten*—The data given in Table XIII show that tungsten interferes seriously in the precipitation of titanium (and zirconium) by cupferron.

TABLE XIII

EXPT. No.	$ZrO_2.TiO_2$ Taken G.	H_2SO_4 Per cent by Volume	Tartaric Acid G.	WO_3 Taken G.	Vol. of Solution Cc.	Weight of Cupferron Ppt. G.	Error G.
1	0.2114	10	None	None	400	0.2114	0.0000
2	0.2114	5	None	0.1266	400	0.2663	+0 0519
3	0.2114	20	None	0.1286	400	0.3043	+0.0929

The ignited oxides in Expts. 2 and 3 were pale blue in color and contained tungsten. It was found that the use of an ammonium hydroxide wash solution markedly lowered the contamination but did not completely eliminate it.

(*l*) *Titanium from Thorium*—The experiments performed at this Bureau and given in Table XIV demonstrate that it is not possible to separate titanium (and zirconium) from thorium by the cupferron method.

TABLE XIV

EXPT. No.	$ZrO_2.TiO_2$ Taken G.	H_2SO_4 Per cent by Volume	Tartaric Acid G.	ThO_2 Taken G.	Vol. of Solution Cc.	Weight of Cupferron Ppt. G.	Error G.
1	0.2114	10	1	None	400	0.2116	+0.0002
2	0 2114	10	1	0.02	400	0.2181	+0.0067
3	0.2114	10	1	0.05	400	0.2288	+0.0174
4	0 2114	10	1	0.20	400	0.2734	+0.0620

(*m*) *Titanium from Cerium*—Quadrivalent cerium interferes markedly in a cupferron precipitation of titanium (and zirconium) while trivalent cerium interferes but slightly. Data obtained in these separations are given in Table XV.

TABLE XV

EXPT. No.	$ZrO_2.TiO_2$ Taken G.	H_2SO_4 Per cent by Volume	Tartaric Acid G.	Ce_2O_3 Taken G.	CeO_2 Taken G.	Vol. of Solution Cc.	Weight of Cupferron Ppt. G	Error G.
1	0.2114	10	1	None	0.02	400	0.2140	+0.0026
2	0.2114	10	1	None	0.05	400	0.2139	+0.0025
3	0.2114	10	1	0.02	None	400	0.2121	+0.0007
4	0.2114	10	1	0.05	None	400	0.2130	+0.0016

(4) INTERFERING SUBSTANCES—It will be noted from the foregoing review that there is a formidable array of interfering elements. These may be divided under five heads, as follows:

(*a*) Interfering elements removable by a preliminary ammonium hydroxide precipitation. Alkalies, alkaline earths, and copper (incompletely) are in this class.

(*b*) Interfering elements removable by hydrogen sulfide in acid solution. These are copper, lead, silver, mercury, tin, bismuth, and other likely interfering elements of the hydrogen sulfide group.

(*c*) Interfering elements removable by ammonium sulfide in ammonium tartrate solution. Iron is the chief element, although this treatment also removes other elements, such as nickel, cobalt, and manganese.

(*d*) Interfering elements removable by the use of an ammonium hydroxide wash. Copper is the chief interfering element of this class. The interference of tungsten and vanadium is lessened by this treatment.

(*e*) Interfering elements not removable. This list includes zirconium, thorium, cerium in the quadrivalent state (less in the trivalent condition), uranium in the quadrivalent condition (but not in the sexivalent state), tungsten, vanadium in either quadri- or quinquivalent condition, and silica. Phosphorus interferes but slightly in a 10 per cent sulfuric acid solution.

(5) SUMMARY—The determination of titanium in pure solutions by the cupferron method is most exact. The method is subject to so many interferences that it loses its value in technical analysis except for certain separations, such as, for example, titanium from chromium and aluminum which are indicated under (3).

ZIRCONIUM

(1) HISTORICAL—Schroeder[1] stated that zirconium could be quantitatively precipitated by cupferron in acid solutions. Thornton and Hayden[2] demonstrated that the determination could be carried out in solutions containing from 5 to 7.5 per cent by volume of sulfuric acid. Ferrari[3] also showed that zirconium could be quantitatively determined in acid solution by means of cupferron. Brown[4] applied the method described by Thornton and Hayden to the analysis of zircon and baddeleyite with excellent results.

Tests, which are given in Table XVI, carried on at the Bureau of Standards, show that zirconium can be quantitatively precipitated in solutions containing 40 per cent by volume of sulfuric acid and that tartaric acid is without effect.

TABLE XVI

EXPT. No.	ZrO_2 Added G.	H_2SO_4 Per cent by Volume	Tartaric Acid G.	Vol of Solution Cc.	ZrO_2 Found G.	Error G.
1	0.1118	5	None	400	0 1118	0.0000
2	0.1118	10	None	400	0.1117	−0.0001
3	0.1118	15	None	400	0.1120	+0.0002
4	0.1118	20	None	400	0.1123[1]	+0 0005
5	0.1118	40	None	400	0 1123[1]	+0.0005
6	0.1118	5	1	400	0 1116	—0.0002
7	0.1118	10	5	400	0.1117	—0 0001

[1] Ignited precipitates contained traces of SO_3.

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[1] *Z. anorg Chem.*, **72** (1911), 89.

[2] *Am. J. Sci*, **38** (1914), 137.

[3] *Ann. chim. applicata*, **2** (1914), 276.

[4] *J. Am. Chem Soc.*, **39** (1917), 2358.

(2) FAVORABLE PROCEDURE FOR PRECIPITATION—The conditions given under TITANIUM 2, governing the precipitation of titanium, apply directly to zirconium.

(3) SEPARATIONS WHICH HAVE BEEN STUDIED. (*a*) *Zirconium from Aluminum*—Data obtained by Thornton and Hayden are given in Table XVII and show a satisfactory separation.

TABLE XVII

EXPT. No.	ZrO_2 Taken G.	Al_2O_3 Taken G.	ZrO_2 Found G.	Error Mg.	H_2SO_4 1 : 1 Cc.	Vol. of Solution Cc.
1	0.1091	0.1127	0.1090	—0.1	40	400
2	0.1088	0.1127	0.1090	+0.2	40	400
3	0.1086	0.1127	0.1090	+0.4	60	400
4	0.1091	0.1127	0.1094	+0.3	60	400

(*b*) *Zirconium from Iron*—The above authors applied the tartrate ammonium sulfide separation of iron, followed by cupferron precipitation of zirconium, and obtained excellent results as shown in Table XVIII.

TABLE XVIII

EXPT. No.	ZrO_2 Taken G.	Fe_2O_3 Taken G.	ZrO_2 Found G.	Error Mg.	H_2SO_4 1 : 1 Cc.	Tartaric Acid G.
5	0.1088	0.1018	0.1091	+0.3	40	2
6	0.1090	0.1018	0.1093	+0.3	40	2

(*c*) *Zirconium from Phosphorus*—Thornton and Hayden claimed that this separation was not feasible.

Experiments carried on at this Bureau and also by Mr. Holladay[1] demonstrated that fair separations are possible if the acidity is high, 10 per cent sulfuric acid by volume, and the concentration of phosphorus pentoxide is not higher than 0.02 g. per 400 cc. of solution. Higher concentrations of phosphorus pentoxide require prior removal, or analysis and correction of the weighed precipitate. Table XIX gives data obtained at this Bureau.

TABLE XIX

EXPT. No.	ZrO_2 Taken G	P_2O_5 Taken G.	Tartaric Acid G.	Weight of Ppt. G.		Error G.	H_2SO_4 Per cent by Volume	Vol. of Solution Cc.
1	0.1118	0.01	None	0.1151	A	+0.0033	5	400
2	0.1118	0.01	1	0.1135		+0.0017	5	400
3	0.1118	0.02	None	0.1123	B	+0.0005	10	400
4	0.1118	0.02	5	0.1121		+0.0003	10	400

Qualitative tests showed considerable phosphorus pentoxide in A and traces in B.

(*d*) *Zirconium from Iron and Aluminum*—Thornton and Hayden obtained very satisfactory separations of these elements, as shown in Table XX, by first separating the iron as described in *b* above and then the aluminum as in *a*.

TABLE XX

EXPT. No.	ZrO_2 Taken G.	Fe_2O_3 Taken G.	Al_2O_3 Taken G.	ZrO_2 Found G.	Error Mg.	Tartaric Acid G.	H_2SO_4 1 : 1 Cc.	Vol. of Solution Cc.
7	0.1087	0.1018	0.0564	0.1086	—0.1	2	40	400
8	0.1089	0.1018	0.0564	0.1088	—0.1	2	40	400
9	0.1101	0.2036	0.1127	0.1110	+0.9	2	40	400
10	0.1100	0.2036	0.1127	0.1103	+0.3	2	40	400

(*e*) *Zirconium from Platinum*—The observation of Thornton concerning the effect of chloroplatinic acid on a cupferron precipitation of titanium, which is given under TITANIUM 3*c*, will undoubtedly hold true for zirconium.

(*f*) *Zirconium from Boric Acid*—See TITANIUM 3*f*.

(*g*) *Zirconium from Alkali Salts*—Thornton and Hayden gave data, tabulated in Table XXI, which show that moderate excess of alkali causes no difficulties. See also TITANIUM 3*g*.

TABLE XXI

EXPT. No.	ZrO_2 Taken G.	K_2O Taken G.	ZrO_2 Found G.	Error Mg.	H_2SO_4 1 : 1 Cc.	Vol. of Solution Cc.
11	0.1088	2.7027	0.1097	+0.9	40	400
12	0.1089	2.7027	0.1096	+0.7	40	400

(*h*) *Zirconium from Silica*—See TITANIUM 3*h*.

(*i*) *Zirconium from Vanadium*—See TITANIUM 3*i*.

(*j*) *Zirconium from Uranium*—See TITANIUM 3*j*.

(*k*) *Zirconium from Tungsten*—See TITANIUM 3*k*.

(*l*) *Zirconium from Thorium*—See TITANIUM 3*l*.

(*m*) *Zirconium from Cerium*—See TITANIUM 3*m*.

(4) INTERFERING SUBSTANCES—The elements which interfere with titanium also interfere with zirconium, except phosphorus which exercises a greater disturbing effect. The methods of removing the interfering elements also apply to zirconium.

(5) SUMMARY—The determination of zirconium in pure solutions by the cupferron method is most exact. The method is subject to so many interfering elements that it loses much of its value in technical analysis. The data given in this chapter demonstrate that the ignited and weighed cupferron precipitate must be most carefully tested in order to make certain of its true composition.

THORIUM

(1) HISTORICAL—Thornton[1] found that precipitation of thorium by cupferron is incomplete in the presence of even a small excess of sulfuric acid. This observation was confirmed at this Bureau. The data given in Table XXII were obtained by Thornton by precipitation in acetic acid solution and by the use of a one per cent ammonium acetate wash.

TABLE XXII

EXPT. No.	ThO_2 Used G.	ThO_2 Found G.	Error G.	Ammonium Acetate G.	Vol. of Solution Cc.	H_2SO_4 (approx.) 1 : 1 Cc.
1	0.0925	0.0924	—0.0001	15	500	1.25
2	0.0923	0.0917	—0.0006	15	500	1.25

(2) FAVORABLE PROCEDURE FOR PRECIPITATION—This is given in Table XXII.

(3) SEPARATIONS WHICH HAVE BEEN ATTEMPTED. (*a*) *Thorium from Iron*—Thornton showed that a good separation of thorium from iron could be obtained by the procedure which he used in similar titanium and zirconium separations (see TITANIUM 3*b* and ZIRCONIUM 3*b*) and gave the data presented in Table XXIII.

TABLE XXIII

EXPT. No.	ThO_2 Used G.	Fe_2O_3 Used G.	ThO_2 Found G.	Error G.	Ammonium Acetate G.	Acetic Acid	Vol. of Solution Cc
3	0.0924	0.1018	0.0922	—0.0002	25	Concentration not stated	400
4	0.0924	0.1018	0.0916	—0.0008	25		500
5	0.1846	0.1018	0.1840	—0.0006	25		400

(4) INTERFERING SUBSTANCES—The elements listed under titanium (see TITANIUM 4) as interfering affect also the precipitation of thorium, and undoubtedly many more on account of the low permissible acidity.

(5) SUMMARY—The determination of thorium by the use of cupferron is of no practical importance since it is affected by as many interfering elements as an ammonium hydroxide precipitation of this element.

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[1] Private communication.

[1] *Am. J. Sci.*, **42** (1916), 151.

VANADIUM

(1) HISTORICAL—Rodeja[1] showed that acid solutions of the alkali metavanadates give a red precipitate somewhat soluble in water. 0.000001 g. of vanadium per cc. gives a reddish coloration changing to green. The author claims that this is a more sensitive qualitative reaction than the potassium sulfocyanate or hydrogen peroxide reactions.

Rodeja[2] in another paper claims that cupferron does not quantitatively precipitate vanadic salts in dilute acid solutions but does precipitate vanadyl salts.

Turner[3] in an attempt to separate vanadium from uranium found that a metavanadate was completely precipitated by cupferron in 1 per cent solutions of hydrochloric or sulfuric acids. The precipitate was washed with one per cent sulfuric acid containing 1.5 g. cupferron per liter and then ignited to V_2O_5. His results are shown in Table XXIV.

TABLE XXIV

Expt. No.	V_2O_5 Taken G.	V_2O_5 Found G.	Error G.
1	0.1655	0.1655	+0.0003
2	0.1655	0.1657	+0.0002
3	0.1655	0.1652	—0.0003
4	0.1655	0.1658	+0.0003

Table XXV gives data obtained by Turner which led him to conclude that Rodeja's statement concerning the incomplete precipitability of vanadic salts by cupferron was incorrect.

TABLE XXV

Expt. No.	V_2O_5 Taken G.	V_2O_5 Found G.
15	0.0873[1]	0.0873
16	0.0882[1]	0.0882
17[3]	0.2300[2]	0.2300
18	0.1952[2]	0.1954

[1] V_2O_5 not reduced before precipitation.
[2] V_2O_5 reduced before precipitation.
[3] Filtrate from this experiment showed vanadium.

(2) FAVORABLE CONDITIONS FOR PRECIPITATION—From the foregoing work it appears that quantitative determinations of vanadium by cupferron can be obtained in one per cent hydrochloric or sulfuric acid solutions of the element in either the quinquivalent or quadrivalent condition provided the precipitate is washed with one per cent acid containing cupferron.

(3) SEPARATIONS WHICH HAVE BEEN ATTEMPTED. (*a*) *Vanadium from Phosphorus*—Rodeja[4] claimed that a satisfactory separation can be accomplished by acidulating with sulfuric acid, boiling with sulfur dioxide to reduce the vanadium, expelling the sulfur dioxide with carbon dioxide, precipitating with cupferron, washing with very dilute sulfuric acid, and igniting to vanadium pentoxide.

(4) INTERFERING SUBSTANCES—Since very dilute acidity only is permissible many elements will interfere in this determination. See THORIUM 4.

(5) SUMMARY—It is certain that the use of cupferron for the quantitative determination of vanadium will find application only in very rare cases.

SUMMARY

The present status of cupferron as a quantitative precipitant is as follows:

1—Cupferron has been successfully used for the quantitative determination of copper, iron, titanium, zirconium, thorium, and vanadium.

2—Many elements interfere with the determinations. In any given determination the partial or complete precipitation of copper, iron, titanium, zirconium, thorium, and vanadium must be considered in addition to the following known interfering elements: lead, silver, mercury, tin, bismuth, cerium thorium, tungsten, uranium in the quadrivalent condition, silica, vanadium, and in certain cases when present in excessive amounts, phosphorus, alkali salts, and alkaline earths.

3—The cupferron method should not be employed unless the qualitative composition of the material to be analyzed is known, or a most careful quantitative examination of the ignited and weighed cupferron precipitate is made.

4—Cupferron can be used advantageously in certain separations, such as iron from manganese, and iron and titanium from aluminum and manganese.

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[1] *Anales soc. españ. fis. quim.*, **12** (1914), 305; *Chem. Abs.*, **9** (1915), 2201.

[2] *Anales soc. españ. fis. quim.*, **12** (1914), 379; *Chem. Abs.*, **9** (1915), 2202.

[3] *Am. J. Sci.*, **41** (1916), 339; **42** (1916), 109.

[4] *Loc. cit.*

BORIC ACID MODIFICATION OF THE KJELDAHL METHOD FOR CROP AND SOIL ANALYSIS[1]

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Received October 20, 1919

In 1913 Winkler[2] proposed the substitution of boric acid for sulfuric acid in the fixation of ammonia distilled over in the course of the Kjeldahl method for the determination of total nitrogen. He tried both methyl orange and congo red as indicators, the results with the latter being slightly better than the former as the following figures show:

METHYL ORANGE INDICATOR

N HCl	8.28 cc.	0.1410 g. NH_3
N HCl	8.27 cc.	0.1408 g. NH_3
N HCl	8.25 cc.	0.1405 g. NH_3
		Av., 0.1407 g. NH_3

CONGO RED INDICATOR

N HCl	8.27 cc.	0.1408 g. NH_3
N HCl	8.21 cc.	0.1398 g. NH_3
N HCl	8.22 cc.	0.1400 g. NH_3
		Av., 0.1402 g. NH_3

The ammonia present was equal to 0.1400 g. The fixing solution in this case consisted of 5 g. boric acid dissolved in 100 cc. distilled water.

Adler[3] in 1916 published a modification of the method adapted to the use of laboratories of the brewing industry, but as it has been impossible to obtain a copy of the original we have had to take our information regarding his work from abstracts.[4] No data regarding his results are given but only an outline of his recommendations for the modification of Winkler's method. He used 50 cc. of a 4 per cent solution of pure crystallized boric acid in the receiving flask. The condenser tube was allowed to remain below the surface of the absorbing solution for the first 15 min. but after that it was raised so that the subsequent distillate served to rinse the end of the tube. The distillate should reach the absorption flask at room temperature. Adler found that 20 min. of vigorous boiling sufficed to distil all the ammonia. In order to obtain maximum accuracy in titration it was necessary to employ a color standard; this was prepared by treating 250 cc. distilled water with 0.15 cc. of 0.1 *N* sulfuric acid and a few drops of methyl orange. The orange-yellow tint remained unchanged for a long time. The distillate, treated with the same amount of methyl orange, was titrated with 0.1 *N* sulfuric acid to the same tint, and the ammonia content calculated from the volume of acid required, no correction being necessary for the boric acid present. The maximum amount of ammonia which was absorbed without loss by the quantity of boric acid mentioned above (50 cc. of 4 per cent solution) was not determined, but it exceeded 70 mg. The results were as accurate as when sulfuric acid was used for absorbing the ammonia.

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[1] Published by permission of the Secretary of Agriculture.

[2] *Z. angew. Chem.*, **26** (1913), 231.

[3] *Z. ges. Brauw.*, **29** (1916), 161, 169.

[4] *J. Inst. Brewing*, **22** (1916), 50; *Chem. Abs.*, **11** (1917), 3371.

In laboratories where it is necessary to run a great number of nitrogen determinations, this modification is of special value because it requires only one standard solution, and since the absolute amount of boric acid in the receiving flask need not be accurately measured, an unskilled assistant may do this part of the work; this rough measurement of the acid saves from one-fourth to one-third of the time necessary to obtain equally accurate results by the old methods. Where the acid solution is made so that 1 cc. equals 1 mg. of nitrogen or some whole number multiple of this figure, the worker can read his results directly from the burette or else obtain them by the simplest mental arithmetic. For these reasons we have experimented with the method as a possible substitute for the one commonly used for the determination of total nitrogen in crops and soils.

SOLUTIONS

The standard sulfuric acid solution was made up so that 1 cc. equaled 1 mg. of nitrogen. The boric acid solution was made by weighing out 4 g. of the acid for each 100 cc. of distilled water used in preparing the 10-liter quantities. The boric acid was dissolved in water at room temperature.

Three indicators were employed: methyl orange, congo red, and bromophenol blue. With the first two it was necessary to make up solutions containing the regular quantity of indicator in 150 cc. of water and sufficient acid to produce the color to be used for a match in the regular titration. The methyl orange was prepared in the usual way by dissolving one gram in 1000 cc. water; congo red, 1 part in 100 parts of 30 per cent alcohol. One-tenth gram of the bromophenol blue was heated with 3 cc. of 0.05 *N* sodium hydroxide till dissolved and then diluted to 250 cc. with distilled water. The end-point of the bromophenol blue was observed by arranging an electric bulb within about 5 in. of a white surface near the burette stand in such a way that the flask during the titration was between the bulb and the reflecting surface; under these conditions the end-point was the disappearance of the purple color. The change is sharp and distinct.

APPARATUS

The apparatus employed for these tests was an unmodified Kjeldahl digestion shelf and distilling stand with condensing tank.

EXPERIMENTS

AMMONIUM SULFATE—The method was first tested by distilling known quantities of nitrogen as ammonia into both sulfuric acid and boric acid. For this purpose a solution of ammonium sulfate containing approximately 0.5 mg. of nitrogen per cc. was used. Fifty cc. of this solution were pipetted into each of the Kjeldahl flasks and 200 cc. of distilled water and 50 cc. of saturated sodium hydroxide solution added. The resulting solution was boiled for 30 min. so that about 150 cc. of distillate passed over, and then 5 min. longer to allow for clearing the delivery tubes.

Two sets of 8 flasks each were titrated with congo red as an indicator, 3 drops being used in each determination; in one set 50 cc. sulfuric acid solution and in the other 50 cc. boric acid solution were used in the receiving flask. The excess sulfuric acid was titrated with ammonium hydroxide, 1 cc. of which equaled 1.011 cc. sulfuric acid.

In order to make the results with the two absorbing solutions comparable, we added 3 drops of congo red to 200 cc. of distilled water and then added 0.30 cc. of acid to produce the same color as was obtained with 150 cc. distilled water, 50 cc. 4 per cent boric acid and 0.35 cc. of standard acid. In the former case, as the end-point comes while the solution is still acid, the correction of 0.30 cc. was added to the burette reading for ammonia to reduce it to what would be obtained if the end-point were taken at the neutral point with this indicator. To correct for the presence of the boric acid it was necessary to subtract 0.35 from the burette reading for sulfuric acid. Two additional sets of distillates in boric acid were titrated, one with bromophenol blue, 3 drops, and the other with methyl orange, 3 drops; in each case the correction constant was 0.3 cc., which was subtracted from the figures obtained for each determination as shown.

TABLE I—NITROGEN RECOVERED FROM $(NH_4)_2SO_4$ SOLUTION

	SULFURIC ACID FIXING AGENT	BORIC ACID FIXING AGENT		
	Congo Red Mg.	Congo Red Mg.	Bromophenol Blue Mg.	Methyl Orange Mg.
	26.20	26.15	26.20	26.10
	26.20	26.25	26.25	26.25
	26.15	26.25	26.25	26.25
	26.25	26.25	26.20	26.25
	26.15	26.15	26.10	26.10
	26.10	26.05	26.25	26.20
	26.25	26.15	26.25	26.15
	26.10	26.25	26.10	26.20
Av.,	26.18	26.19	26.20	26.19

PROCEDURE WITH CROPS AND SOILS—The crops were weighed, placed in a Kjeldahl flask, and 30 cc. concentrated sulfuric acid containing 10 per cent phosphoric anhydride and 0.5 g. of anhydrous copper sulfate added before starting the digestion. The digested material in the acid was diluted with 175 cc. of distilled water and treated with 100 cc. concentrated sodium hydroxide and a few pieces of mossy zinc. The distillates from these solutions were received in approximately 50 cc. portions of 4 per cent boric acid and titrated with standard sulfuric acid, using bromophenol blue as an indicator. This indicator was selected in preference to any of the others because when used under the conditions described for observing the end-point, the disappearance of the purple color (which could also be observed through a screen as in hydrogen-ion determinations) is sharper and more distinct than either of the others and has the added advantage that it is not necessary to keep a color standard for comparison.

The soils were digested in 40 cc. of concentrated sulfuric acid containing 1 g. of salicylic acid in each 25 cc. The soil is allowed to digest half an hour at room temperature, then 0.5 g. of iron or zinc dust is added, and after standing half an hour longer 5 g. of Lipman's sulfate mixture[1] is added and the digestion completed over the flame. After digestion, when the solution has cooled sufficiently, distilled water is added and the liquid contents of the flask transferred to another Kjeldahl flask and the residue well washed with distilled water which is also transferred to the second flask. The water added should not be much over 175 cc. One hundred cc. of saturated caustic soda and some mossy zinc are then added and the solution distilled into boric acid and the distillate titrated the same as the distillate from crops.

Following the procedures outlined, first with the reagents employed for crops and for soils, and later with crops and soils, the figures shown in Table II were obtained.

TABLE II—NITROGEN FOUND IN CROPS AND SOILS

SUBSTANCE	Weight G.	Flask No.	Titration Corrected for Indicator Cc.	Less Check Cc.	Average Cc.
Reagents for Crops	..	1	0.10	...	
		2	0.10	...	
		3	0.10	. .	
		4	0.10	. .	0.10
Reagents for Soils	..	1	0.40	...	
		2	0.40	...	
		3	0.30	...	
		4	0.30	...	0.35
Corn Fodder	1	1	5.80	5.70	
		2	5.60	5.50	
		3	5.65	5.55	5.58
Corn Fodder	2	1	11.50	11.40	
		2	11.50	11.40	
		3	11.50	11.40	11.40
Wheat Grain	1	1	22.35	22.25	
		2	22.30	22.20	
		3	22.30	22.20	22.22
Wheat Grain	2	1	44.60	44.50	
		3	44.60	44.50	
		2	44.45	44.35	44.45
Sweet Clover	1	1	28.35	28.25	
		2	28.60	28.50	
		3	28.60	28.50	28.42
Sweet Clover	2	1	57.00	56.90	
		2	57.00	56.90	
		3	57.10	57.00	56.93
Soil No. 1	10	1	4.05	3.70	
		2	4.00	3.65	
		3	4.10	3.75	3.70
Soil No. 2	10	1	4.55	4.20	
		2	4.40	4.05	
		3	4.50	4.15	4.13

In tests with an ammonium sulfate solution it was found that when 50 cc. of 4 per cent boric acid solution were used 05 mg. of nitrogen as ammonia could be recovered with accuracy. This result was obtained without the use of glycerin which Adler recommends.

SUMMARY

Winkler's modification of the Kjeldahl method in which he proposed the use of boric instead of sulfuric acid in the receiving flask is found to be as accurate as when the latter reagent is employed. Ninety-five mg. of nitrogen as ammonia can be recovered in the distillate when 50 cc. of 4 per cent boric acid is used.

Bromophenol blue is a better indicator than those used by the other investigators.

The method has the following advantages:

1—It does away with the occasional errors that arise from slight mistakes in measuring the sulfuric acid into the receiving flask.

2—As the boric acid solution need be measured only approximately, much time can be saved, and an unskilled helper can measure it into the receiving flasks.

3—By proper adjustment of the strength of the standard acid and the weights of the samples taken the percentage of nitrogen can be read directly from the burette.

4—It is necessary to prepare accurately only one standard solution, *i. e.*, the sulfuric acid for titrating.

A RAPID AND ACCURATE METHOD FOR DETERMINING NITROGEN IN NITRATE OF SODA BY THE MODIFIED DEVARDA METHOD AND THE USE OF THE DAVISSON SCRUBBER BULB[1]

By C. A. Butt

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There is among chemists with whom I have come in touch, and especially among those engaged in the fertilizer industry, a very strong conviction that the usual methods for the determination of nitric nitrogen, as in the analysis of nitrate of soda, are far from satisfactory for routine work and none too accurate in the hands of the average analyst. Procedures used in the average fertilizer works laboratory should of necessity be both rapid and accurate; moreover, it is very desirable that constant attention be not required. The modified Kjeldahl-Gunning method, which had been used in our laboratory for several years, produced fairly satisfactory results, provided considerable time were given to complete the solution and reduction of the nitrate in the salicylic acid mixture. In addition to this time-consuming procedure, agreeing duplicate determinations have been very difficult to obtain, unless the sample be dried and ground very fine. Naturally, therefore, our attention was turned to other direct methods.

The Devarda method, as refined in late years by W. S. Allen[2] and also E. R. Allen,[3] appeared the most promising, as both investigators obtained almost theoretical results. The method recommended by W. S. Allen, while very accurate, necessitated the use of the modified Knorre apparatus which was rather elaborate and more complicated as to operation than seemed desirable.

The procedure outlined by E. R. Allen for nitric nitrogen in soil extracts, which he designated as the Volmari-Mitscherlich-Devarda method, seemed more suitable in that the reduction and distillation were effected in a very dilute alkali solution which permits the reaction to proceed quietly, a distinct advantage over other methods in which strong alkali solutions are used. E. R. Allen found that one gram of 60-mesh alloy was sufficient to reduce 25 mg. nitric nitrogen in 300 cc. of approximately 0.1 *N* NaOH, reduction and distillation being completed in 40 min., using the modified Mitscherlich apparatus in which the water cooling is dispensed with and the ammonia absorbed by passing the steam through a scrubber into the receiving flask.

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[1] K_2SO_4, 20 parts; $FeSO_4$, 2 parts; $CuSO_4$, 1 part.

[1] Presented before the Fertilizer Division at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 4, 1919

[2] *8th Intern. Congr. Appl. Chem.*, **1** (1912), 19.

[3] THIS JOURNAL, **7** (1915), 521

By using the E. R. Allen method in this laboratory in connection with the regular Kjeldahl rack without a scrubber, favorable results were obtained, provided the reaction was allowed to proceed with gentle heat for several hours and the distillation then completed over a low flame. Even then at times we found that the alkali mist would be carried into the tube of the condenser, thereby rendering blank tests variable.

None of these procedures, therefore, seemed simple or rapid enough until the Davisson[1] type of scrubber came to our notice. This scrubber bulb is built similarly to and may be substituted for the Hopkins connecting bulb where the necessity arises for a scrubber for the ammonia vapors. Davisson found that the entrained alkali can be satisfactorily removed when the vapors are scrubbed through water previous to condensation. According to his statement, the first steam which passes into the scrubber condenses on the surface of the bulb and flows down about the small bulb and there acts as a scrubbing solution for the remaining vapors. This solution is neutral or slightly alkaline, and the long period of steam distillation removes all the ammonia.

When using this scrubber in connection with the modified Devarda method, it was found in this laboratory that since the alkali mist passed into the condenser tube before any condensation occurred in the bulb it was necessary to draw about 20 cc. of water by suction into the scrubber before beginning the distillation.

A large number of the solutions left in the scrubber at the end of the distillation period have been tested with Nessler's reagent. Out of a total of more than 30 solutions, only 2 have shown the reaction for ammonia and these showed only a very faint coloring. Likewise a large number have been tested by the phenolsulfonic acid method,[2] and in no case were nitrates found.

To determine whether or not any alkali passes the scrubber, ammonia-free water and sodium hydroxide were used in blank tests on three separate occasions, and the distillate titrated, one drop of 0.1 *N* sulfuric acid being sufficient in all cases to produce a distinct color change with methyl red indicator. This confirms Davisson's statement that thorough scrubbing of the vapors is accomplished.

The method used in this work is based on the findings of W. S. Allen, who recommended using 3 g. of Devarda's alloy to 1 g. of nitrate of soda, and the findings of E. R. Allen, who verified Volmari's conclusions that approximately 0.1 *N* sodium hydroxide solutions are sufficiently concentrated for the reduction and distillation, and that strongly alkaline solutions cause the reaction to be so violent that care must be continually exercised to prevent a loss of the determination.

The Devarda's alloy used in this work was obtained from J. T. Baker, and upon testing was found to be ammonia-free. A fineness test on the original sample showed: 100 per cent passing 10-mesh sieve, 76 per cent passing 20-mesh sieve, 19 per cent passing 60-mesh sieve.

To determine the effect of the degree of fineness on the results a few determinations were carried out using in one determination 3 g. of alloy remaining on 20 mesh and in the duplicate 3 g. of the alloy passing 20 mesh with the following results:

Test Number	Alloy Remaining on 20 Mesh Per cent Ammonia Found	Alloy Passing 20 Mesh Per cent Ammonia Found
1	19.97	19.96
2	19.96	19.98
3	18.85	18.82
4	18.81	18.81

These results indicate that an alloy passing a 10-mesh sieve is sufficiently fine under the conditions of the method to be outlined.

The time required for complete reduction and distillation was also studied. Tests were made, distilling 15, 30, 45, and 60 min. The results follow:

Minutes Distilling	15	30	45	60
Per cent ammonia found	16.21	18.49	18.99	19.03

To the contents of the flasks containing the condensate from an additional 15 min. distillation, one drop of 0.1 *N* sulfuric acid gave a distinct color change with methyl red indicator. This shows that one hour's reduction and distillation is sufficient for a practically complete recovery of the nitrogen.

METHOD OF ANALYSIS

The method in detail recommended for the analysis of nitrate of soda is as follows:

PREPARATION OF SAMPLE—The sample should be put through a 10-mesh sieve and mixed thoroughly. This we have found to be sufficiently fine to obtain good duplicate checks. Out of a total of 23 samples analyzed since adopting this procedure, duplicate determinations have shown the following agreements: 35 per cent within 0.05 per cent NH_3, 78 per cent within 0.10 per cent, and all within 0.15 per cent.

DETAILS OF MANIPULATION—Weigh 17.034 g. and transfer to a 500 cc. volumetric flask (calibrated to correspond with the pipette to be used) and add 300 cc. of water. Warm to dissolve, cool, and make up to mark. After mixing thoroughly, pipette 25 cc., corresponding to 0.8517 g. of sample, into a Kjeldahl flask of 500 to 650 cc. capacity. Add 300 cc. of water, 3 g. Devarda's alloy (75 per cent of which will pass 20-mesh sieve), 3 to 5 cc. 45° Bé. sodium hydroxide, and connect at once with the Kjeldahl distilling apparatus fitted with the Davisson scrubber into which has been drawn 20 to 30 cc. of water. Conduct distillation of the ammonia synchronously with the reduction, regulating the boiling so that 175 to 200 cc. of distillate is collected in about one hour. When distillation is about half completed, it is recommended that part of the solution in the scrubber be sucked back into the distilling flask, allowing 10–20 cc. to remain in the bulb, this being accomplished by removing the flame or holding the flask out of place a moment while still connected. This removes the danger of the liquid splashing into the condenser tube, and by reducing the volume in the bulb facilitates the passing of the last traces of ammonia into the receiving flask.

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[1] THIS JOURNAL, **11** (1919), 465.

[2] Scott, "Standard Methods of Chemical Analysis," **1917**, p. 539.

Twenty-one cc. of 0.5 *N* sulfuric acid are used in which to absorb the ammonia and the titration is carried out as in the regular Kjeldahl method, using methyl red indicator.

Cc. 0.5 *N* acid required = per cent ammonia

ACCURACY OF METHOD—0.5 *N* sulfuric acid used in the following work was carefully standardized by the sodium carbonate method.[1] This solution in a series of tests averaged within 0.03 per cent of the theoretical ammonia equivalent of specially prepared and dried ammonium sulfate when ammonia in the salt was determined by the above method.

0.25 *N* sodium hydroxide was prepared by titration against the 0.5 *N* H_2SO_4 using methyl red indicator.

A check sample of sodium nitrate was prepared from C. P. sodium carbonate and nitric acid, free from chlorides and sulfates, recrystallized and dried at 150° C. Upon analysis this salt showed the following:

H_2O	0.08 per cent
NaCl	0.02 per cent
KNO_3	0.62 per cent
Na_2SO_4	Trace
Fe_2O_3	Trace
Al_2O_3	Trace
CaO	Trace
MgO	Trace
SiO_2	Trace

Correcting for the K_2O found and deducting from 100 per cent all the impurities the result is 99.80 per cent sodium nitrate. The theoretical ammonia, therefore, equals 20.00 per cent.

Results which were obtained at various times on this check sample are as follows:

No.	Per cent Ammonia Found	No.	Per cent Ammonia Found	No.	Per cent Ammonia Found
1	19.99	5	20.03	9	19.95
2	20.00	6	19.95	10	19.96
3	19.99	7	19.96	11	19.99
4	20.04	8	19.98	12	19.99
Highest			20.04		
Lowest			19.95		
Average			19.99		

It will be noted the extremes show a variation of 0.09 per cent ammonia, equivalent to 0.45 per cent sodium nitrate. Blank determination showed an equivalent of 0.01 per cent ammonia, which was deducted from all results.

The effects of the presence of sodium chloride and also sodium carbonate were then determined with results as follows:

AMOUNTS ADDED TO ALIQUOT IN FLASK BEFORE DISTILLING

No.	NaCl 0.04 g. Added Per cent Ammonia Found	NaCl 1 g. Added Per cent Ammonia Found	No.	Na_2CO_3 0.04 g. Added Per cent Ammonia Found	Na_2CO_3 1 g. Added Per cent Ammonia Found
1	20.03	19.94	6	20.02	19.92
2	20.04	19.94	7	19.97	19.97
3	19.93	19.99	8	20.00	19.89
4	20.00	20.03	9	20.02	20.03
5	19.99	20.02	10	19.99	19.99
Av.	20.00	19.98	Av.	20.00	19.96

The foregoing figures indicate that neither of these compounds in quantities of 1 g. or less has an appreciable effect on the results.

In order to show whether or not the same degree of accuracy is attainable on commercial nitrate of soda, two samples were selected at random from a lot arriving at the laboratory, and each was run in duplicate by three analysts. Following are their results:

ANALYST	Sample 1 Per cent Ammonia Found	Sample 2 Per cent Ammonia Found
1	18.79	18.97
	18.83	18.93
Average	18.81	18.95
2	18.82	18.97
	18.78	18.98
Average	18.80	18.98
3	18.83	19.00
	18.84	19.01
Average	18.84	19.01

Upon making analyses on these two samples for all impurities and using the average ammonia figures for Sample 1, 18.82 per cent, and Sample 2, 18.98 per cent, the following shows that the method had yielded exceptionally accurate results:

	Sample 1	Sample 2
H_2O	3.08	2.74
Insoluble	0.21	0.26
Na_2SO_4	0.27	0.33
NaCl	0.51	0.56
$NaClO_3$	0.05	0.05
$NaClO_4$	0.94	0.51
Fe_2O_3 Al_2O_3	0.10	0.09
CaO	0.09	0.07
MgO	0.18	0.10
$NaIO_3$	0.05	0.04
P_2O_5	0.04	0.06
KNO_3	3.48	2.55
$NaNO_3$	90.98	92.57
TOTAL	99.98	99.93

	Sample 1	Sample 2
$NaNO_3$ by modified Devarda method	93.92	94.72
$NaNO_3$ by deducting from 100 per cent all impurities and correcting for the K_2O found	93.93	94.78

SUMMARY

The modified Devarda method as outlined, used in connection with the regular Kjeldahl rack, fitted with the Davisson scrubber, in addition to being rapid, is capable of producing exceptionally accurate results and is suitable for routine work. Reduction and distillation may be completed in one hour.

The presence of 1 g. of sodium chloride or sodium carbonate in the sample is shown to have no appreciable effect on the determination.

Ten- to twenty-mesh alloy is shown to be sufficiently fine under the conditions of the method outlined.

In view of the excellent results obtained it is hoped that the fertilizer division will include this procedure or a modification of the same in any work that may be carried out toward the improvement in our methods for nitrate of soda analysis.

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[1] Scott, *Loc. cit.*, p. 503.

TESTING THE STRENGTH OF GLUE JELLEIS

By Wilson H. Low
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Received September 8, 1919

Testing of the strength of glue jellies has been carried on in this laboratory for a great many years, and under the direct supervision of the writer for the last 21 years. In that time all kinds of devices have been used for this purpose, but until the Smith glue tester (Fig. 1) came out, there was none on the market sensitive enough to show even fairly large differences or to duplicate the "finger test" so valuable in the hands of an expert.

This form of tester is far superior to any other we have seen, but in its original form the testing, although sensitive enough, was subject to some errors which affected the grading of the glues. Moreover, since it was filled simply with water colored with a dye to make it visible on the scale, glues were often met with which could not be measured on the scale. The only modification of the Smith glue tester that we have seen illustrated is that of E. C. Hulbert[1] (Fig. 3).

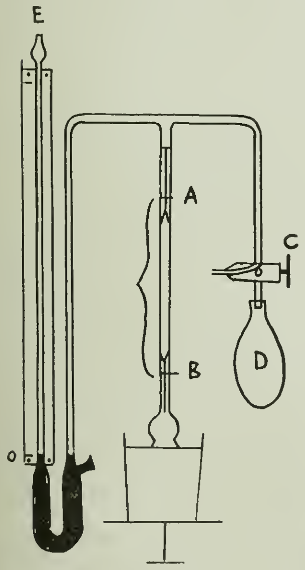

Fig. 1

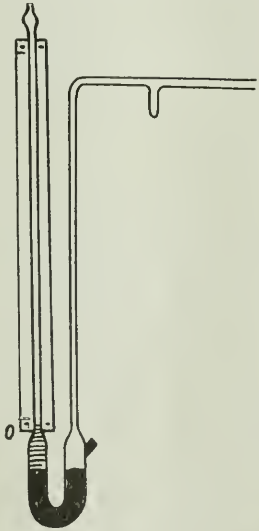

Fig. 2

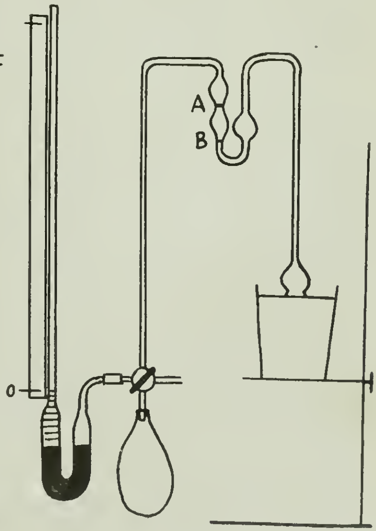

Fig. 3

The principal modifications are the use of mercury covered by water in the scale tube, and the use of air, instead of water, in the thistle tube, the mouth of which is covered with a thin, dental rubber diaphragm, as in the original Smith glue tester.

The use of mercury is a distinct improvement and has been followed in this laboratory for years. We do not readily see the advantage of the substitution of air for water in the thistle tube, especially since leaks are not so easily noticed in the rubber diaphragm or where it is attached to the thistle tube.

The apparatus used in this laboratory (Fig. 2) consists of a Smith glue testing apparatus modified to give more accurate results for grading glues correctly. Mercury is used in the U-tube, and above this colored water. The scale has slots at each end to allow of moving it and setting it by the screws that fit through the slots. All other parts of the instrument are as illustrated in Fig. 1.

It was first determined by calculation and experiment that the use of mercury covered by water in the scale tube gave correct results. It was found necessary to correct for the force required to deform the diaphragm itself, for this takes some force that should not be credited to the jelly, and this force is not a constant, for diaphragms vary much with different rubbers and vary from day to day through permanent stretch of the rubber. Another point is that it is necessary to find the force required to deform the rubber when the instrument is set in the position for a test, that is, when the water stands at point A in the diagrams.

Owing to changes in temperature of the water and mercury in the instrument or of the whole instrument, the water will not always stand at the zero mark of the scale, as it should in starting a test. To overcome this trouble we made our scale movable in a vertical direction. With these modifications and methods of application we found we could properly grade our glues or glue jellies very closely and with comparative correctness.

METHOD OF USE

Our instrument is kept permanently in a chill room connected with the laboratory and maintained close to 40° F., at which temperature the glue jellies are tested; that is, the jellies are at the same temperature as the room and close to 40° F. Standard glues of various grades are always run at the same time, so temperature or other changes affecting the strength will act on the standards and jellies being tested in like manner. Enough water is put into the thistle tube and capillary so that when a flat glass plate is held firmly against the mouth of the thistle tube (covered with the rubber diaphragm) the water in the capillary will stand exactly at the upper mark A, the three-way stopcock C being opened to the air. Stopcock C is now closed to the air and opened to the rubber bulb D and scale tube E, the water in which was set to the zero mark. Pressure is now applied through the bulb (a screw clamp between the bulb and stopcock allowing only a steady, slow, and even pressure to be applied to the system) until the water in the capillary falls from the point A to the point B. The height of the water in the scale tube is now read off, and this measures the force required to deform the rubber diaphragm alone, and this force must be deducted from the tests on the jellies for the proper grading of the glues. If all joints of the instrument are tight, the stopcock C may be closed as soon as the water reaches the point B, and the height of the water in the scale tube read off at leisure, but this cannot be done unless everything is absolutely tight.

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[1] This Journal, 5 (1913), 235.

To test a jelly in a tumbler, as illustrated, the stopcock is opened to the air and it is ascertained that the water in the scale tube stands at the zero mark. The tumbler is placed on the movable support shown (by coarse screw adjustment) and brought in contact with the rubber diaphragm and forced against this diaphragm until the water in the capillary stands at the point A. The stopcock C is then quickly closed and immediately the rubber bulb is squeezed steadily and the water in the capillary forced down to the point B. The height of the water in the scale tube is now quickly read and measures the force required to deform the jelly by a definite volume, namely, the volume between points A and B on the capillary tube. It also includes the force required to deform the rubber alone, so for the force required by the jelly itself, the figure previously found for the rubber must be deducted. It is necessary to operate with moderate speed in adjusting the jelly surface to the rubber diaphragm and in forcing down the water from A to B. This should be done by a steady, even pressure, not by jerky or quick application of pressure on the bulb.

Used correctly this instrument is very sensitive and gives concordant results. Used incorrectly it is still sensitive, but will not give concordant results. The water in the capillary *must* stand at the point A when a flat glass or metal plate is held firmly against the mouth of the thistle tube covered with the rubber, as only in this way can we start with the jelly and rubber forming an approximately flat surface. It is assumed generally that if the mouth of the thistle tube is forced against the jelly surface until the water in the capillary stands at point A we are starting under like pressures each time. But this is not so. It makes a difference whether we press into the jelly so that it forms a convex surface upwards into the rubber and then force down to a flat surface at the end, or whether we start with a level surface on the jelly and force the rubber downward into the jelly. In the first case the jelly itself tends to return to its original position and acts with the rubber, in the other case it continually works against the rubber.

An attempt was made to use an artificial jelly surface by stretching a rubber diaphragm over the mouth of the tumbler through the side of which we made a hole and attached a long pressure measuring tube. The tumbler was then completely filled with water and pressures through the thistle tube applied to the rubber surface. This did not work at all, for the rubber of the tumbler not only was deformed through the thistle tube, but bulged up between the center and sides and the pressures recorded were not at all proportional to the pressures applied. This same thing undoubtedly occurs to some extent in testing a glue jelly and occasions errors, but to no such extent as with a liquid like water acting on an elastic diaphragm. Working against a mercury surface was also unsatisfactory for several reasons. In short, nothing has been found to replace running a set of standard grades with each set of tests.

DETERMINATION OF THE TENSILE STRENGTH OF GLUE[1]

By George Hopp

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At the present time the testing of glue consists for the most part in the determination of the viscosity and jelly strength, as compared to a standard glue. This standard glue is usually one which has been selected because of the satisfaction it has given through years of practice. In the purchasing of glue, manufacturers hesitate considerably in departing from a particular standard, because of their lack of knowledge of how another glue will act. As six to ten months may elapse before the manufacturer knows the results, it is quite obvious that considerable risks may be run. The question also arises as to whether the standard adopted is what it should be for a particular type of work, whether it has the requisite strength or elasticity, is brittle or the reverse.

Various methods of measuring the tensile strength have been tried, such as gluing together wood or biscuit ware, or soaking paper in glue and determining the strength of the glues. These have been unsuccessful, due to the presence of so many variables, such as humidity, temperature, viscosity and temperature of glue, pressure at which it is applied at the joints, and condition of the joints, such as the amount of moisture, smoothness of surface, etc. Recognizing the fact that the most important test of a glue should be a knowledge of its actual strength and stretch or elasticity, and that equipped with such knowledge, standards could then be scientifically established for every phase of work, a new method has been evolved.

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[1] Presented at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

This work was originally done in 1913–1914, but owing to the fact that there were no suitable tensile machines at hand, the completion of the work was put off till this time.

METHOD

The method consists in melting the glue, pouring into molds, drying, cutting into strips of definite size, and obtaining the strength and stretch by pulling on a tensile machine.

Solutions of glue, 60 to 80 per cent by volume, are soaked for 12 hrs. and melted up at a temperature of 160° F. Great care is necessary at this point to avoid the formation of bubbles and foam.

The molds are of irons, 12 in. square and $^1/_4$ in. deep. The surface of the iron is carefully polished, so that no impression of any kind will be left on the glue. It should be noted that the slightest imprint becomes strongly emphasized on the dried glue surface. The mold is just warm enough to prevent chilling of the glue, approximately 130° F. The glue solution is poured into the leveled molds and permitted to jell. Under summer conditions, approximately 5 hrs. are allowed. This sheet is then removed and permitted to dry on fine-meshed galvanized or tinned wire, raised so as to permit circulation of the air around the under surface of the glue. The glue sheet is continually reversed in order to obtain a flat surface without too much curling. As soon as the edges show signs of complete drying, they are cut to prevent curling and the formation of uneven spots and strains. This cutting consists merely of making a slit about $^1/_4$ in. deep into the glue. By drying under slight pressure as soon as the glue appears partially dried, a perfect flat surface is obtained. It should be noted that the jellying and drying should take place undisturbed by air currents of any kind. The flat sheet is next cut into strips of definite size, preferably using a hot knife, as this is considerably quicker than using a very sharp cutter. They are then ground exactly on a grinding wheel or other suitable device. The center portion of the strip is then ground in, to insure breaking at center. The thickness of the strips and the widths were varied in order to check up the results. A suitable thickness averaged 0.1 in. and a suitable width 0.33 in. The overall length of the strip was about 7 in. and the ground portion at center about 2.5 in. A strip is illustrated in the accompanying photograph.

The tensile machine was an electrically driven Schopper with a capacity of 500 kg. The jaws on this machine are more nearly in alignment than on any other machine used. This is of vital importance, as the slightest deviation of the jaws will give poor results, due to the torsion and shear set up.

RESULTS

Using a hide glue, designated D-400, the following tests covering several parts of a shipment were made:

Thickness	Width	Kg. Break	Per cent Stretch	Tensile Strength Lbs. per Sq. In.
0 091	0.337	174	3	12,510
0.077	0.352	168	3	13,690
0.088	0.352	185	3.0	13,200
0.144	0.411	362	3.5	13,500
0.096	0.382	216	3.5	13,000
0.099	0.398	235	5	13,200
0.094	0.399	226	4.5	13,270
0.091	0.446	249	5	13,500
0.097	0.379	218	...	13,100
0.103	0.425	262	5.5	13,180
0.147	0.403	368	6	13,710
0.102	0.426	259	5.5	13,150
0.139	0.433	358	5	13,270
0.095	0.345	198	4.5	13,350
0.130	0.322	248	...	13,100
0.102	0.444	269	6	13,100
0.098	0.459	271	6.5	13,300
			Av.,	13,240

The following are the results obtained with a glue designated D-300:

Thickness	Width	Kg. Break	Per cent Stretch	Tensile Strength Lbs. per Sq. In.
0.057	0.352	75	2	8,250
0.054	0.355	76	2	8,750
0.055	0.350	71	2	8,150
0.057	0.336	73	1.9	8,400
0.061	0.346	83	2	8,690
0.095	0.351	137	2.8	9,050
0.095	0.349	123	2.2	8,200
0.055	0.314	68	2	8,700
			Av.,	8,523

A glue designated A-500 and taken from various portions of a shipment averaged 7,600 lbs. per sq. in. and 2 per cent stretch. A glue designated G-"Special" averaged 11,573 lbs. per sq. in. and 3.5 per cent stretch.

These glues were kept under standard conditions but pulled at room temperatures. They represent glues in commercial use of 3 different factories, and were selected because of the ease with which they could be obtained.

DISCUSSION

It will be noted that the results check very closely. Using varying widths and thicknesses, the tensile strength was always about the same. The stretch showed slight variation, due largely to the inaccuracy of the scale readings.

CONCLUSIONS

This method gives a feasible way of determining the exact strength and stretch of a glue, its elastic limit and other physical properties. It will permit manufacturers to determine exactly the physical character and properties of their glues, also to vary their processes and raw materials and determine the effect on the finished product.

This method will also permit the establishment of scientifically selected standard expressed in absolute units. At present it is not possible to compare the results of tests made by one laboratory with those of another, as the strength of solution, temperature, and manipulation are different. There are often exceptions to the fact that a glue with a high viscosity or jelly strength is stronger than a low viscosity glue

Certain factories can often meet viscosity and jelly requirements of a sample, but their glues will lack the strength and flexibility of glues from other factories having exactly the same jelly and viscosity.

At the present time work is being done to determine the following:

1—The relationship between the viscosity, jelly strength, tensile strength, and stretch.

2—The relationship between gelatin, chondrin, keratin, mucin, etc., and their effect on the strength and stretch of a glue.

3—Effect of heating and the length of time of heating on the strength and stretch of glues, both in liquid form and dried form

4—Effect of the soaking of glues on their strength and stretch.

5—Effect of the age of glues on their strength and stretch.

6—Effect of dissolving a glue, drying, redissolving, etc., on the strength and stretch.

7—Effect of the addition of other substances to glue.

8—Effect of humidity and temperature on glue.

THE DETERMINATION OF IODIDE AND BROMIDE IN MINERAL WATERS AND BRINES[1]

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In a former paper[2] the authors recommended the permanganate method for the determination of iodide in mineral waters and brines. By the use of this method the iodide is oxidized to iodate by potassium permanganate in slightly alkaline solution and the iodate determined iodometrically by adding potassium iodide, acidifying with hydrochloric acid and titrating the liberated iodine with thiosulfate. This method gives very satisfactory results for the iodide content, but it does not leave the solution in a condition suitable for the determination of the bromide content.

In that paper the authors also showed that iodide may be quantitatively separated from large amounts of chlorides (up to 10 g. NaCl) and from amounts of bromide equivalent to not more than 0.3 to 0.4 g. bromine by liberating the iodine with ferric sulfate and removing it by distillation with steam. The iodine is absorbed in a potassium iodide solution and titrated with thiosulfate.

In a second paper[3] a method was proposed for the estimation of bromide in the presence of large amounts of chloride (10 g. NaCl). This method takes advantage of the selective oxidizing action of chromic acid, and the liberated bromine is removed by aspiration.

In the present paper some results are reported of determinations of the iodide and bromide content of mixtures of iodide, bromide, and chloride. These results were obtained by combining the ferric sulfate method for iodide with the chromic acid method for bromide.

PROCEDURE

The procedure for the determination of iodide and bromide in the presence of chloride is as follows: The iodide should first be determined by the permanganate method, since more accurate results can be obtained by its use than by the use of the ferric sulfate method. Another sample is then taken which should contain not more than 0.1 g. of bromine as bromide or more than 10 g. of total salts. The iodine is removed from this sample by oxidizing with ferric sulfate and distilling the liberated iodine with steam according to the method described in the first paper. The iodine is absorbed in a potassium iodide solution and may be titrated with thiosulfate and the results used to check those obtained by the permanganate method. The residue in the distilling flask is emptied into a beaker, heated to boiling, and the iron precipitated with ammonia or sodium hydroxide. If sodium hydroxide is used, care must be taken not to add a great excess, though a slight excess will be taken care of later by the chromic acid. Any excess of ammonia will be removed during the subsequent evaporation. Filter off the iron hydroxide, wash with hot water, and evaporate to dryness or nearly so. The bromide is determined in the residue by the chromic acid method, the details of which were given in the second paper.

Calcium chloride does not interfere with either determination, but care should be taken when precipitating the iron not to precipitate too much calcium hydroxide by the addition of an excess of alkali, as otherwise the precipitate will be bulky and difficult to wash. This applies also to magnesium chloride if sodium hydroxide is used for precipitating the iron. If much magnesium chloride is present the solution may become acid during evaporation, due to hydrolysis. This may be guarded against by coloring the solution with methyl orange and adding a drop of sodium hydroxide solution if it becomes acid.

Expt. No.	NaCl Taken G.	I as KI Taken G.	Br as KBr Taken G.	I Found G.	Br Found G.	Error in I Det. G.	Error in Br Det. G.
1	..	....	0.0600	....	0.0598	....	—0.0002
2	..	....	0.0800	....	0.0798	....	—0.0002
3	10	....	0.0800	....	0.0790	....	—0.0010
4	..	0.0803	0.0800	0.0794	0.0798	—0.0009	—0.0002
5	10	0.0803	0.0200	0.0792	0.0191	—0.0011	—0.0009
6	10	0.0803	0.0400	0.0794	0.0385	—0.0009	—0.0015
7	10	0.0402	0.0800	0.0397	0.0784	—0.0005	—0.0016
8	10	0.0803	0.0800	0.0792	0.0790	—0.0011	—0.0010
9	10	0.0803	0.0200	0.0795	0.0188	—0.0008	—0.0012
10	10	0.0803	0.0400	0.0798	0.0385	—0.0005	—0.0015
11	10	0.0803	0.0020	0.0805	0.0015	+0.0002	—0.0005
12	10	0.0803	0.0040	0.0798	0.0033	—0.0005	—0.0007
13	10	0.0803	0.0010	0.0792	0.0006	—0.0011	—0.0004
14	10	0.0402	0.1000	0.0396	0.0984	—0.0006	—0.0016

An inspection of the table will show that the results for iodide are all low with the exception of Expt. 11, which is probably due to an error of manipulation. Much better results can be obtained by the use of the permanganate method. The results for bromide are also low, but it is believed that this method will give more accurate results for the bromide content of such mixtures than any other method.

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[1] Read before the Division of Water, Sewage and Sanitation, at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 5, 1919.

[2] This Journal, 11 (1919), 563.

[3] *Ibid.*, 11 (1919), 954.

LABORATORY AND PLANT

AUTOMATIC METHODS OF GAS ANALYSIS DEPENDING UPON THERMAL CONDUCTIVITY[1]

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Received August 19, 1919

PRINCIPLE OF THE METHOD

When a wire, surrounded by a gas enclosed in a space the walls of which are at constant temperature, is continuously traversed by a constant electrical current, the wire rises in temperature until a state of equilibrium is reached. in which the continuous dissipation of thermal energy is equal to the electrical energy supplied. This dissipation of energy takes place in the four following ways:

1—By radiation.

2—By conduction through the connections to the ends of the wire.

3—By thermal convection, *i. e.*, by currents of gas circulating in the atmosphere surrounding the wire.

4—By conduction through the gas.

In case there is a flow of gas past the wire, heat is also carried away by the gas stream.

By a proper choice of conditions, all loss of heat except by conduction through the gas surrounding the wire may be reduced to a small portion of the whole. The equilibrium temperature attained by the wire will then depend mainly upon the thermal conductivity of the gas which surrounds the wire, being lower when the gas has a high conductivity and higher when the gas has a low conductivity. Since the coefficients of thermal conductivity of various gases and gas mixtures differ widely (Table I), the temperature of the wire will be determined by the composition of the surrounding gas. If, now, the wire has a high temperature coefficient of electrical resistance, its resistance to the passage of a constant current of electricity, depending as it does on the temperature of the wire, will have a value corresponding to the thermal conductivity, and therefore to the composition of the surrounding gas or gas mixture.

Table I—Thermal Conductivity of Gases
(From Smithsonian Physical Tables)

Gas	$k_t \times 10^4$
Air	0.568
Argon	0.389
Ammonia	0.458
Carbon monoxide	0.499
Carbon dioxide	0.307
Ethylene	0.395
Helium	3.39
Hydrogen	3.27
Methane	0.647
Nitrogen	0.524
Nitrous oxide	0.350
Oxygen	0.563

(k_t is the heat in gram-calories flowing in 1 sec. through a distance of 1 cm. per sq. cm. for 1° C. drop in temperature.)

Inasmuch as electrical circuits are easily arranged for the rapid and very accurate determination or comparison of the resistance of such a wire, the quantitative determination of the constituents in a wide variety of gas mixtures whose qualitative compositions are known is possible by a simple and exceedingly sensitive method based upon the thermal conductivity of the mixtures.

HISTORY OF THE METHOD

Schleiermacher[1] developed a method for determining the thermal conductivities of gases by utilizing the fact that a platinum or nickel wire stretched along the axis of a glass tube immersed in a water bath assumes a temperature, when heated by an electric current of constant strength, which depends upon the nature of the gas surrounding the wire. Goldschmidt[2] improved Schleiermacher's original method by comparing two wires of different lengths inclosed in silver capillaries inserted in a massive brass block. This improved method was used by Eucken[3] in his experiments on the thermal conductivity of gases. The use of thermal conductivity for gas analysis was probably first suggested by Leon Sowzee about 1880. Unfortunately a description of his method is not available since the report of the Prussian Fire Damp Commission, in which the only known reference to it occurs, gives no details. The Vereinigte Maschinenfabrik, Augsburg, patented in Germany[4] and England[5] the use of the thermal conductivity of a gas containing hydrogen to obtain an indication or a record of the variation in composition of a gas mixture. Several devices are specified, in one of which the resistance of an electrically heated wire in a closed tube is measured. This firm appears, however, to have been unsuccessful in applying the method. A. Koepsel[6] developed an apparatus for the determination and continuous indication of the hydrogen content of producer gas, which he stated was capable of easily detecting the presence of 0.001 per cent of hydrogen without the use of very refined measuring apparatus. He also proposed the application of his apparatus to the determination of carbon dioxide in flue gases and of methane in mine gases, but did not demonstrate experimentally the feasibility of his proposals. In its most improved form, Koepsel's apparatus consisted of four electrically heated wires exposed in pairs to the two gases to be compared. the two wires of each pair being connected to form opposite arms of a Wheatstone bridge. Koepsel's apparatus was particularly designed for use in a rather rapid gas stream and rather elaborate housings were arranged for the wires to shield them from the effects of convection. Siemens and Halske[7] improved Koepsel's apparatus by passing the gases going to the two sides of the bridge through tubes in the same metal block to bring them to the same temperature, and eliminated Koepsel's special housing for the wires.

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[1] Published by permission of the Director of the Bureau of Standards.

[1] *Wied. Ann.*, **34** (1888), 623; **36** (1889), 346.

[2] *Physik. Z.*, **12** (1911), 417.

[3] *Ibid.*, **12** (1911), 1101.

[4] D. R. P. 165,349 (1904).

[5] Brit. Patent 15,706 (1904).

[6] *Ber. physik. Ges.*, **10** (1908), 814; **11** (1909), 237; *Z. Chem. apparat.*, **3** (1908), 377, 401; *Chem. Abs.*, **2** (1908), 3212; **3** (1909), 1108, 2646.

[7] D. R. P. 283,677 (1913).

In 1915 or 1916 the Sperry Gyroscope Company developed an apparatus similar to that of Siemens and Halske for detecting hydrogen in air. About the same time, but before learning of the work of this company, some investigations along the same line were begun at the Bureau of Standards but were abandoned because the delicacy of the indicating instrument required made it unsuitable for the immediate purpose in view. In the first months of 1917 a gas analysis apparatus utilizing the thermal conductivity principle was developed by a group of men at the University of California, was submitted to the Navy Department, and was tried out successfully for a number of purposes. In this instrument, which was extremely simple, two arms of the Wheatstone bridge consisted of wires stretched in the axes of metal tubes and exposed to the gases to be compared; the other two arms of the bridge were fixed external resistances. Prof. G. A. Shakespear[1] of Cambridge, England, has developed an apparatus similar in principle to that of the "University of California Hydrogen Detector," though of more compact construction, small platinum coils being substituted for the straight wires used in the earlier instrument.

As far as it is known, these investigators confined their methods to the use of a Wheatstone bridge with fixed resistances, depending upon the deflection of a galvanometer or millivoltmeter for indicating the relative resistance of the heated wires exposed to the gas to be analyzed and to a "standard gas," usually air.

About the first of January 1918, work was begun at the Bureau of Standards to utilize a thermal conductivity method in connection with a number of problems, and in addition to the schemes used by the other investigators, a number of other combinations were tried; and what is believed to be the most generally useful form of apparatus was arrived at by a process of elimination.

The history of this development is given in such detail in order to clear up a situation which might otherwise give rise to ill feeling. It is known that one of the recent experimenters believed himself the first to utilize heat conductivity measurements for making gas analyses until his apparatus was submitted to the Bureau of Standards for test, and a similar claim has been repeatedly made for another investigator, though not by the investigator himself.

In July 1918, at the request of the Nitrate Division of the Ordnance Department of the Army, the solution of the problem of the continuous analysis of the gases was undertaken for the analytical control of the synthetic ammonia plant being erected at Sheffield, Alabama. It was planned to use the thermal conductivity method for much of this work. At the time of the signing of the armistice when work on the ammonia plant was discontinued, the apparatus had been constructed and calibrated and was practically ready for installation in the plant.

The feasibility of using the method for the continuous analysis of the gases at different stages in the separation of helium from natural gas was indicated by a few experiments. At the request of the Navy Department, this application of the method was developed, and apparatus for determining and automatically recording the percentage of helium in helium-nitrogen mixtures was built, calibrated, and installed in one of the helium extraction plants where it is reported to have given very satisfactory service for several months. Work has started on the construction of equipment for a 16-point analytical control apparatus for installation in another helium plant.

As opportunity has offered, experiments have been made to ascertain the applicability of the method to various important industrial processes. The uniform success which has been obtained indicates that its field of usefulness extends to a large number of operations and processes where a knowledge of changes in composition of gas mixtures is desired.

DESCRIPTION OF ELECTRICAL ARRANGEMENTS

WHEATSTONE BRIDGE WITH INDICATOR—In the device suggested by Koepsel[1] the indications of the changes in composition of a gas mixture were obtained in the following manner: Four wires of like material, cross-section, and length constituted the arms of a Wheatstone bridge. Two of the wires, forming opposite arms of the bridge, were placed together in a cell through which passed a current of the gas for analysis; the other two wires were placed together in a cell through which passed a comparison gas. Thus the differences in thermal conductivity of the gases in the two cells resulted in a maximum of unbalance of the bridge. An instrument calibrated to indicate directly the percentages of a constituent of the gas mixture of variable composition replaced the customary galvanometer. Since the resistance of the wire is very materially affected by changes in the current strength, the current must be carefully adjusted and maintained at a definite value. Koepsel used a battery as a source of constant current and avoided the use of an additional current-measuring instrument by providing a resistance coil between the battery and the bridge across the terminals of which the indicator could be switched. Current through the bridge was adjusted by means of a rheostat in the battery circuit until the deflection of the pointer of the indicator reached a certain mark on the scale. Fig. 1 shows diagrammatically the arrangement of the apparatus.

This arrangement, which is essentially the same as that developed by the other investigators mentioned, has many limitations. In order that the apparatus may detect small changes in the composition of the gas mixture, the indicator must have a high sensitivity, making it a necessarily expensive instrument, and since there must be a special scale for each gas and each range of gas percentages if the apparatus is to indicate percentages of the desired constituent directly, it becomes impracticable to use the same instrument for the determination of more than a very few constituents in a gas mixture and only over a small number of ranges. Furthermore, the usefulness of apparatus for the analysis of gas mixtures whose composition is continuously changing is frequently dependent upon whether the apparatus can be arranged to provide a record of the changes in gas composition, to actuate control mechanisms, or to positively sound an alarm. For these purposes neither Koepsel's apparatus nor any other apparatus utilizing the same type of bridge arrangement is suited.

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[1] U. S. Patent 1,304,208 (1919).

[1] *Loc. cit.*

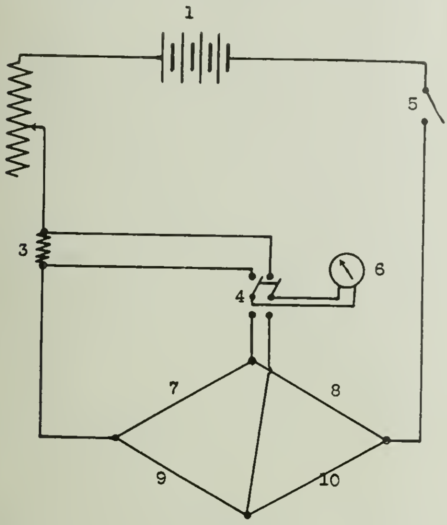

Fig. 1

1—Battery
2—Rheostat
3—Drop coil (shunt)
4—Double knife, double throw switch
5—Switch
6—Indicator
7, 10—Wires exposed to gas mixture
8, 9—Wires exposed to comparison gas

BALANCED BRIDGE ARRANGEMENT—These and other considerations led to the adoption of a balanced bridge arrangement in the method devised at the Bureau of Standards. Two wires, preferably of like material, cross-section, and length, stretched along the axes of two tubes in the same metal block, constitute two arms of a Wheatstone bridge. A Kohlrausch slide wire, such as is used in measurements of the conductivity of electrolytes, together with extension resistances ("end coils") form the other two arms. A portable, inexpensive, d'Arsonval needle galvanometer is used to indicate the balance point. The gas mixture to be analyzed is passed through the tube containing one of the wires; a comparison gas having a constant composition, such as air or hydrogen, and having a thermal conductivity of the same order as that of the gas mixture, or else the residual gas mixture after a constituent has been removed is passed through the tube containing the other wire. The bridge is balanced by moving the contact on the slide wire until the galvanometer gives a zero reading. After the apparatus has been calibrated the position of the contact on the slide wire is an indication of the relative resistances of the two wires and of the presence and amount of one or more constituents of the gas mixture. Thus, the expensive specially calibrated galvanometer of small range or close scale is in effect replaced by a uniformly divided slide wire of very large range and wide open scale as the measuring instrument.

In order to determine when the current through the bridge just described is correctly adjusted, a second bridge is connected in series. Three arms of this bridge are fixed resistances, and the fourth arm is a wire, exactly similar to the wires of the first bridge, stretched along the axis of a gas-tight metal tube. Since the resistance of this wire constituting the fourth arm varies greatly with small changes of current, the current is adjusted very accurately when the bridge is balanced. By adjusting one of the fixed resistance arms, the bridge may be made to balance with any desired current strength. Both the conductivity apparatus and the current adjustor are placed in an electrically heated oil bath with thermostat. If desired, the same galvanometer may be used for both current adjustment and the conductivity bridge.

When the limit of variation of the desired constituent of a gas mixture is about 10 or 20 per cent, it has been found that by making the extension coils of the slide wire of the proper resistance, the position of the sliding contact with respect to a uniformly divided scale indicates directly and with considerable accuracy the percentages of the constituent when the bridge is adjusted to give no deflection of the galvanometer needle. Consequently the process of calibration consists of determining the values of the resistances which the two bridge extension coils should have for the constituent and gas mixture in question. The calibration of apparatus for the determination of 0–10 per cent carbon dioxide in air will suffice to illustrate a method for finding the value of the end resistances. Fig. 2 shows diagrammatically the arrangement of the apparatus.

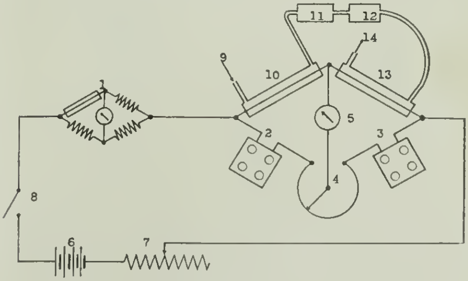

Fig. 2

1—Current adjustment bridge
2, 3—Four dial resistance boxes
4—Slide wire bridge
5—Galvanometer
6—Storage battery
7—Rheostat
8—Switch
9—Entrance for gas mixture
10, 13—Thermal conductivity cells
11—Carbon dioxide absorber
12—Drying tube
14—Exit for residual gas

With the contact of the slide wire bridge (4) set at zero, pure, dry air free from carbon dioxide is allowed to flow at a rate of about 20 cc. per minute through the entrance (9) into the first conductivity cell (10), thence to a carbon dioxide absorber (11), and, after being dried over calcium chloride (12), passes through the second conductivity cell (13) and is discharged at (14). When the gas circuit is thoroughly swept out the switch (8) is closed, the setting of the rheostat (7) is varied until the current adjustment bridge (1) is balanced, and with one resistance box, *e. g.*, (2), set at a definite value, the other resistance box (3) is adjusted until the galvanometer (5) gives no deflection. Care must be taken that the current through the circuit is correct when the final adjustment is made. The settings of the two resistance boxes are noted and by increasing the resistance in (2) by regular steps and obtaining the corresponding values of (3) when the galvanometer (5) gives a zero reading, a series of values of correct end resistances is secured for the lower limit of carbon dioxide content.

A mixture of approximately 10 per cent carbon dioxide—90 per cent air is then prepared in a mercury-sealed gas-holder, carefully analyzed by volumetric apparatus, and then allowed to flow through the gas circuit of the thermal conductivity apparatus as described above for air. With the contact of the slide wire bridge (4) set at the scale division corresponding to the average of the volumetric analyses of carbon dioxide, another series of correct end resistance values for the upper limit of carbon dioxide content is secured.

Choosing the resistances of one box as ordinates and of the other as abscissae, end resistance curves corresponding to the lower and upper limits of carbon dioxide variation are plotted. The intersection of these curves gives the value of the end resistances to be used for this range of variation of the desired constituent in the given gas mixture.

Table II shows two series of end resistance values for a 0–10 per cent carbon dioxide-in-air calibration.

TABLE II—END RESISTANCE VALUES FOR CO_2-IN-AIR CALIBRATION
(Resistance in Ohms)

Box 2	Box 3 0 Per cent CO_2	 10.28 Per cent CO_2
200	170.6—	174.7
300	270.4+	273.6+
400	370.1	372.45
500	469.9	471.4
600	569.6	570.2—
610	579.55	580.1
620	589.55	589.9
630	599.5+	599.8
640	609.5	609.7
650	619.5+	619.55
660	629.4+	629.4
670	639.4	639.3
680	649.4	649.2
700	669.4	669.05

The curves shown in Fig. 3 are plotted from the end resistance values given in Table II. The excellent agreement between analysis by the thermal conductivity apparatus and by careful volumetric analyses of several carbon dioxide-air mixtures is shown in Table III.

TABLE III—ANALYSES OF CO_2-AIR MIXTURES

AVERAGES OF VOLUMETRIC ANALYSES Per cent CO_2	ANALYSIS BY THERMAL CONDUCTIVITY APPARATUS (Uncorrected Reading of Instrument) Per cent CO_2
0.00	0.20
2.65	2.68
4.85	4.85
7.12	7.14
10.28	10.28

By the use of a suitable switch the same slide wire, galvanometer, and current adjustor may be employed in connection with any desired number of thermal conductivity units. It is only necessary to provide special end resistance coils, which are easily and cheaply constructed, with each of the conductivity units to make the apparatus indicate directly the percentages of the constituents in the various gas mixtures for which the instrument has been calibrated.

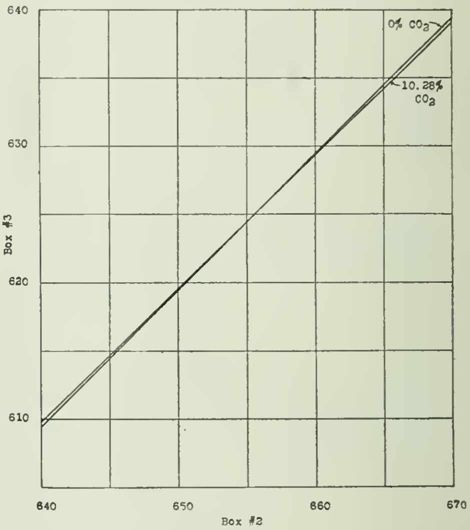

FIG. 3

RECORDER—Unlike the devices used or suggested by others for gas analysis by methods depending upon thermal conductivity, the manually operated arrangement just described may be readily adapted to give a continuous record of gas composition, to actuate plant control mechanism, and to sound an alarm. For these purposes it is only necessary to substitute for the galvanometer and slide wire a recorder of the type manufactured by the Leeds and Northrup Company arranged to adjust automatically the position of a contact on a slide wire until a galvanometer gives no deflection, to draw a curve, or to otherwise provide a record of the position of the contact with respect to the slide wire, and, if desired, to operate mechanical or electrical devices of any suitable construction.

REPRESENTATIVE ANALYSES

In order to indicate the wide applicability of the thermal conductivity method which has been developed and to show the accuracy which has been obtained by its use a series of representative analyses is given below.

HYDROGEN IN HYDROGEN-AIR MIXTURES—The following results were obtained in the calibration of apparatus intended for use in determining the permeability of balloon fabrics to hydrogen. The gas mixture for analysis surrounded one wire of the thermal conductivity apparatus, and pure dry air the other.

Table IV—Analyses of Hydrogen-Air Mixtures

	Analysis by Thermal Conductivity Apparatus	
Analysis by Gas Interferometer Per cent H_2	(Uncorrected Reading of Instrument) Per cent H_2	Analysis from Calibration Curve Per cent H_2
0.096	0.092	0.096
0.150	0.147	0.150
0.207	0.201	0.203
0.204	0.202	0.204
0.231	0.229	0.231
0.278	0.276	0.277
0.406	0.408	0.407
0.556	0.558	0.555
0.704	0.707	0.704
0.846	0.848	0.846
0.962	0.964	0.962
1.175	1.176	1.175

HYDROGEN IN HYDROGEN-NITROGEN MIXTURES—The results given in Table V were obtained on units calibrated for use in the synthetic ammonia plant. The variable gas mixture passed through one thermal conductivity cell and pure hydrogen was used as the comparison gas.

Table V—Analyses of Hydrogen-Nitrogen Mixtures

	Analysis by Thermal Conductivity Apparatus (Uncorrected Reading of Instrument)					
Averages of Volumetric Analysis Per cent H_2	Unit No. 6 Per cent H_2	Unit No. 8 Per cent H_2	Unit No. 9 Per cent H_2	Unit No. 11 Per cent H_2	Unit A Per cent H_2	Unit No. 2 Per cent H_2
67.58	67.58	67.58	67.58	67.58	...	...
69.63	69.85	69.88	69.69	69.69	...	...
72.67	72.67	72.67	72.67	72.67	...	...
75.43	75.44	75.52	...	...	75.41	...
74.00	...	...	...	...	74.00	...
71.40	...	...	...	...	71.40	...
66.50	...	...	...	...	66.50	...
42.48	...	...	...	...	...	42.48
44.65	...	...	...	...	...	44.75
47.62	...	...	...	...	...	47.62
...	65.99	65.87	...	...	...	...
...	66.22	66.28	...	...	...	...
...	69.63	69.75	...	...	...	...
...	71.30	71.35	...	...	...	...
...	74.00	73.93	...	...	...	...

NITROGEN IN NITROGEN-HYDROGEN MIXTURES—Table VI shows analyses made by a unit for the synthetic ammonia plant. Pure hydrogen was used as the comparison gas.

Table VI—Analyses of Nitrogen-Hydrogen Mixtures

Averages of Volumetric Analyses Per cent N_2	Analysis by Thermal Conductivity Apparatus (Uncorrected Reading of Instrument) Per cent N_2
3.43	3.43
5.30	5.35
8.60	8.60

CARBON DIOXIDE IN CARBON DIOXIDE-AIR MIXTURES—Refer to Table III.

CARBON DIOXIDE IN MIXTURES OF HYDROGEN, NITROGEN, AND CARBON DIOXIDE—In Tables VII and VIII are given the results obtained on apparatus calibrated for the synthetic ammonia plant. The apparatus was arranged in the same manner as that described for the determination of carbon dioxide in air. It is to be noted in Table VII that, though the hydrogen-nitrogen ratio of the mixtures has been varied considerably, the analyses of carbon dioxide by the thermal conductivity method are almost unaffected.

Table VII—Analyses of CO_2, Hydrogen, and Nitrogen Mixtures (Unit A)

Hydrogen in Residue Per cent H_2	Nitrogen in Residue Per cent N_2	Averages of Volumetric Analyses Per cent CO_2	Analysis by Thermal Conductivity Apparatus (Uncorrected Reading) Per cent CO_2
40	60	2.42	2.45
40	60	2.53	2.53
40	60	2.79	2.73
40	60	4.55	4.55
40	60	5.30	5.20
40	60	6.90	6.90
40	60	7.69	7.60
40	60	10.05	10.05
37.33	62.67	0.00	0.00
37.33	62.67	1.00	0.90
37.33	62.67	3.29	3.29
37.33	62.67	6.05	6.00
37.33	62.67	8.10	8.27
37.33	62.67	10.03	10.23
29.36	70.64	0.00	0.05
29.36	70.64	2.37	2.30
29.36	70.64	3.67	3.64
29.36	70.64	6.55	6.55
29.36	70.64	10.82	11.07

Table VIII—Analyses of CO_2, Hydrogen, and Nitrogen Mixture (Unit B)

Hydrogen in Residue Per cent H_2	Nitrogen in Residue Per cent N_2	Average of Volumetric Analyses Per cent CO_2	Analysis by Thermal Conductivity Apparatus (Uncorrected Reading) Per cent CO_2
70	30	22.52	22.52
..	..	25.15	25.15
..	..	27.53	27.53
..	..	27.80	27.77

AMMONIA IN MIXTURES OF AMMONIA, NITROGEN, AND HYDROGEN—Ammonia is determined by passing the gas mixture first through one conductivity cell, then through an ammonia absorber, and finally through the second thermal conductivity cell. In Table IX analyses made by two units are given. The residue after the removal of ammonia contained 75 per cent hydrogen and 25 per cent nitrogen.

Table IX—Analyses of Ammonia, Nitrogen, and Hydrogen Mixtures

	Analysis by Thermal Conductivity Apparatus (Uncorrected Readings)	
Averages of Volumetric Analyses Per cent NH_3	Unit No. 10 Per cent NH_3	Unit A Per cent NH_3
0.27	0.39	0.30
2.55	2.52	2.42
2.63	2.65	2.62
5.26	5.20	5.10
5.78	5.63	5.55
8.03	7.96	7.85
8.48	8.36	8.28

HELIUM IN MIXTURES OF HELIUM AND NITROGEN—Helium in mixtures of helium and nitrogen is determined by passing the gas mixture through one thermal conductivity cell while hydrogen is passed through the other cell as a comparison gas. In Table X are shown the uncorrected readings made by a recorder when used in connection with two different thermal conductivity units together with the corresponding analyses made with a gas interferometer.

Table X—Analyses of Helium-Nitrogen Mixtures

	Uncorrected Recorder Readings 0–100 Per cent Range		Analyses from Calibration Curves	
Gas Interferometer Analyses Per cent He	Unit No. 1 Per cent He	Unit No. 2 Per cent He	Unit No. 1 Per cent He	Unit No. 2 Per cent He
9.8	7.1	7.5	9.8	10.0
19.8	21.3	22.5	19.8	20.7
30.0	34.3	34.3	30.0	29.9
40.1	45.0	45.7	40.0	40.2
50.3	54.7	55.0	50.3	50.3
58.4	60.9	61.4	58.3	58.4
63.6	64.7	65.0	63.6	63.3
71.8	70.7	71.2	72.4	72.3
82.7	77.2	77.7	82.7	82.7
87.7	80.2	80.7	87.6	87.6
88.8	81.0	81.8	88.9	89.5
90.5	82.0	82.4	90.8	90.5
93.1	83.2	84.0	93.3	93.1
	80–100 Per cent Range			
82.7	81.7	82.8	82.7	82.7
87.7	88.5	89.8	87.7	87.9
88.8	90.0	91.2	88.9	89.0
90.5	91.7	92.7	90.1	90.1
93.1	95 5	96.7	93.1	93.1

Although the direct readings taken from the recorder chart deviate considerably from the corresponding interferometer analyses, the discrepancies disappear when the direct recorder readings are corrected by means of calibration curves.

CONSTRUCTION OF APPARATUS

THERMAL CONDUCTIVITY UNITS—The thermal conductivity units used in making the representative analyses cited in this paper are a product of evolution. In attempting to eliminate or avoid difficulties encountered in the early forms of construction the present form has resulted. Consequently, though an arrangement has been devised that works surprisingly well, future study will no doubt suggest further improvements.

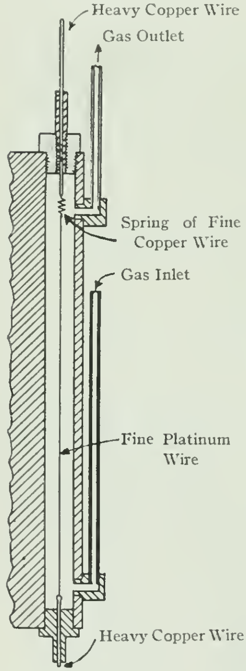

Fig. 4

In order to secure high sensitivity with a small consumption of energy it has been found that the wires exposed to the gas mixture for analysis and to the comparison gas should preferably be of small diameter and made from metals having a high temperature coefficient of resistance. Wires of nickel, tungsten, and platinum of various diameters and lengths have been successfully employed. Platinum, however, on account of its freedom from reaction with most gases, low thermoelectric power against copper, permanence of physical properties, and the ease of fusing it to supporting and connecting terminals, has been selected as the metal usually most suitable. The best diameter and length to choose for the wires depends upon the current strength to be employed and the sensitivity desired. Wires having diameters of 0.0254 and 0.0508 mm. (0.001 and 0.002 in.) and lengths of 15 and 10 cm. (6 and 4 in.) have given ample sensitivity with bridge currents of 0.15 ampere for the smaller wire and 0.30 ampere for the larger wire. In order to concentrate the resistance in the platinum wires, render the connections to the ends of the wires permanent and the junctions free from objectionable thermal e. m. f., copper wires are fused to each end of the platinum wire. To minimize the danger of the wire being displaced from its position when stretched along the axis of the tube forming the conductivity cell, one copper terminal is made of as heavy a wire as can be conveniently fused to the small platinum wire, and the other copper terminal is made of fine copper wire, which, after one end has been fused to the small platinum wire, is wound into a helical spring and the free end is soldered to a heavy copper wire.

The gas chambers in which these platinum wires are stretched consist of two tubes in the same metal block, each provided with a gas inlet and outlet and bushings for supporting the wire stretched along the axis. Brass has been found a suitable metal where noncorrosive gases are used and the tubes are simply cylindrical holes drilled lengthwise through a square brass rod. To minimize the effect on the calibration of any possible displacement of the active wires and to reduce the power required to produce a given temperature difference between the wire and the wall of the tube, the diameter of the tubes or cells is made the maximum permissible. Experiments have shown that when the diameter much exceeds one centimeter convection currents cause unsteady readings. This unsteadiness appears rather suddenly as the diameter of the cell is increased, and the value of the limiting diameter is in somewhat striking agreement with the thickness of the stationary conducting gas film assumed by Langmuir[1] in his discussion of the loss of heat by conduction and convection from a cylindrical surface. Since the electrical arrangement used requires that the wires in the two cells be connected in series, it is necessary to insulate only one end of each wire from the metal block. This insulation is secured by Bakelite bushings screwed into one end of each cell and fitted with brass sleeves to which the wires may be soldered. The bushings are coated with Khotinsky cement to render the joints gas-tight. Fig. 4 shows a section through one of the cells with the active wire in place and Fig. 5 is a photograph of a complete unit.

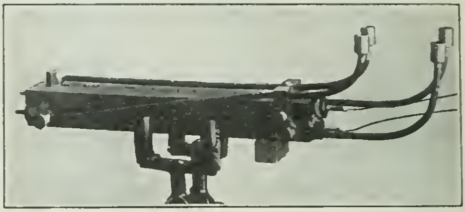

Fig. 5

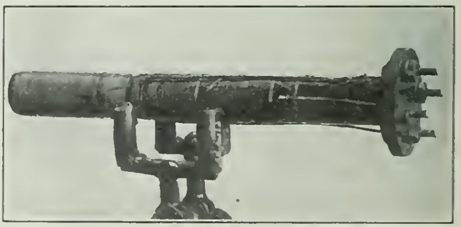

Fig. 6

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[1] *Phys. Rev.*, **34** (1912), 401

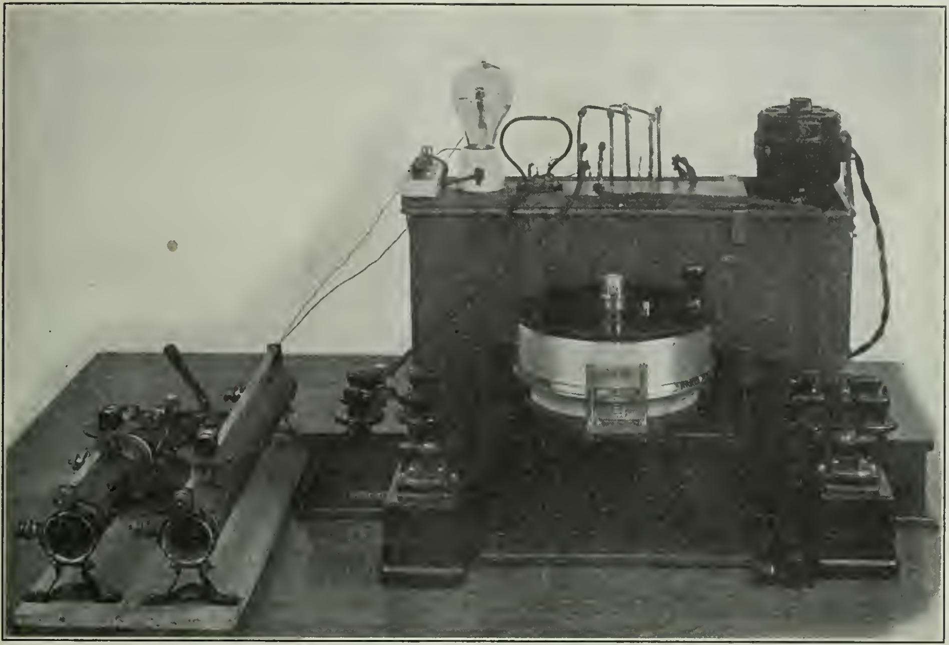

Fig. 7

END RESISTANCE COILS—After the values of the end resistances to be used with a thermal conductivity unit for the determination of a constituent in a gas mixture have been ascertained, as described in connection with the calibration of apparatus for the determination of carbon dioxide in air, the expensive resistance boxes are replaced by inexpensive coils. These coils are wound non-inductively on bobbins with advance or manganin wire, carefully adjusted to the proper resistances, and mounted for convenience in the oil bath together with the thermal conductivity units. A photograph of such a pair of end resistance coils is shown in Fig. 6.

An idea of the appearance of the manually operated apparatus as set up for experimental work on gas analysis by the thermal conductivity method may be had by inspection of the photograph shown in Fig. 7.

EXTENT OF STUDY OF METHOD AND PLANS FOR FUTURE WORK

Owing to the fact that loss of heat from the active wires in the conductivity cells takes place not only by conduction through the gas, but also to some unknown extent by convection, radiation, conduction through the terminals, and heating the stream of gas flowing past the wire, it has been considered inadvisable and not worth while to attempt to determine the mathematical relations which would make possible the calibration of the apparatus by calculation. Experience has shown that the results obtained by empirical calibration are fully as reliable as those given by the apparatus with which the gas mixtures used in calibration are analyzed.

Although it is known in a general way that the readings are steady and reproducible when the rate of flow of the gas mixtures through the cells does not greatly exceed 20 cc. per minute, a careful study of the quantitative effect of changes in bath temperature and variations in bridge current is yet to be made. Plans for future work include the investigation of these effects, a study of the relative thermal conductivities of various gas mixtures, and further development of a number of devices which have already been applied in a preliminary way to the analysis of more complex gas mixtures than those cited, and to the application of the method to recording and automatic control work.

SUMMARY

1—A new form of apparatus for the continuous analysis of gas mixtures by an electrical method depending upon thermal conductivity is described.

2—Unlike the previous deflection methods of limited application, a balanced-bridge method applicable to the rapid and accurate determination of constituents in a wide variety of gas mixtures of industrial importance has been developed.

3—The adaptability of the apparatus for either manual or automatic recording operation is pointed out.

4—Representative analyses showing the results obtained with apparatus constructed for the determination of hydrogen, nitrogen, carbon dioxide, ammonia, and helium in various gas mixtures are given.

5—The construction of the special forms of apparatus required for this method is described.

6—Plans for future work are outlined.

AN EFFECTIVE CONNECTING BULB

By C. M. Clark

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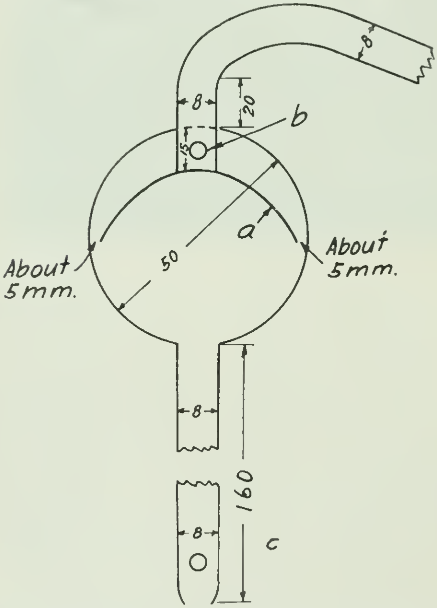
Received November 5, 1919

We have frequent occasion in this laboratory to distil from flasks at a very rapid rate and have many times been troubled by the spray being carried over in spite of the best connecting bulbs we could obtain.



The writer was, in consequence, led to design the bulb herewith illustrated, which has on repeated trials and under the severest conditions fulfilled all requirements. It was first tested by half filling an Erlenmeyer flask with a 10 per cent solution of KOH and catching the distillate in water to which phenolphthalein has been added. Although the boiling was pushed until portions of the liquid were actually carried up into the bulb not a trace of color appeared in the catch water. Under such conditions all other bulbs on the market allowed spray to pass over, coloring the catch water red.

In the figure, *a* is a baffle-plate in the form of a deep watch glass, similar to that used in the "Pistorius" still. It reaches to within about 5 mm. of the sides of the bulb and effectually prevents any spray from reaching the exit holes *b*. Neither the small hole *c* near the lower extremity of the inlet tube, nor the slight narrowing of the end of that tube is essential, but it is believed that they assist in holding back spray. The dimensions given are in millimeters; they are intended to be only approximate, the general dimensions of the bulb being those of similar bulbs now on the market.

APPARATUS FOR THE DETERMINATION OF MELTING POINTS

By L. M. Dennis

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Received November 19, 1919

The most exact method for the determination of the melting point of an organic substance consists in the observation of the melting point and solidifying point of the substance by direct immersion of the thermometer in the partly molten and partly solid mass.[1] This method is, however, frequently impracticable because at least 20 g. of material are necessary for the determination. It has therefore become customary to determine the melting point of an organic substance with approximate accuracy by placing a small amount of the material in a thin-walled glass tube about 1 mm. in diameter, fastening the tube to the side of a thermometer, and heating the thermometer and tube to the temperature at which the sample changes from the solid form to a clear and transparent liquid.

The heating of thermometer and sample tube is usually effected by immersing the two to proper depth in pure, concentrated sulfuric acid and then heating the acid until the melting point of the substance has been reached. It is apparent that if the acid that surrounds the bulb of the thermometer is unevenly heated, the readings may show considerable variation from the true melting point of the substance. For this reason it has been recommended[2] that the temperature be raised very slowly through the last 10°. It is preferable, however, to stir the sulfuric acid while it is being heated, and this can be accomplished either by mechanical stirring with a bent glass rod, or by means of the ingenious device of Olberg[3] in which the heating of the sulfuric acid causes the acid to circulate through the apparatus and thus tends to equalize the temperature throughout the liquid. This tube of Olberg has been simplified by Thiele.[4] The accuracy of a determination of the melting point of a substance with the Thiele tube is largely dependent upon the speed of flow that is set up in the sulfuric acid when the tube is heated. Acceleration of the circulation of the acid will naturally give better results. Very considerable errors that had been made by students in the determinations of the melting points with the Thiele tube seemed to indicate a too slow circulation of the acid.

The Thiele tube is heated at or just below the bend of the side loop.[1] The rise of the warm, specifically lighter acid through the upper side of this loop toward the main tube is, however, retarded by the slightness of the pitch of the tube and its relatively small diameter as compared with that of the upright portion of the tube. This slowness of movement of the acid causes marked differences of temperature of the upper and lower portions of the acid in the upright tube where the bulb of the thermometer and the substance are located, and also retards the even rise of temperature of the acid throughout the apparatus.

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[1] Lindenbaum, "Die Methoden der Organischen Chemie," I. p 193.

[2] Wegscheider, *Chem.-Ztg.*, **29** (1905), 1224

[3] *Repert. anal. Chem.*, **1886**, 95.

[4] *Ber.*, **40** (1907), 996.

With the object of accelerating the circulation of the sulfuric acid and the equalization of temperature throughout the acid, with consequent increase in the accuracy of the results of the determinations, the writer made a tube of the shape shown in Fig. 1, and this and a Thiele tube were subjected to detailed and careful comparison by Mr. Raleigh Gilchrist. The tubes were filled with pure, concentrated sulfuric acid to a point about one cm. above the opening of the upper side-arm D. The temperatures were measured with two Anschütz thermometers which were first carefully compared to ascertain their variation. In the temperature readings that are given in the tables, correction is made for these variations. The thermometer T was so placed that its bulb was opposite the upper opening of the side-arm. The bulb of the other thermometer, S, was 4 cm. below that of T and was slightly to the left of the middle of the larger tube. The thermometers were similarly placed in the Thiele tube. The two tubes were heated with small Bunsen flames 2.5 cm. high, so placed that the tip of the flame was 4.5 cm. below the tube. The Thiele tube was heated on the lower side of the outer bend of the side-arm; the new form was heated slightly to the right of the point marked A. In making comparisons of the tubes, the Bunsen flame was placed in position and readings of the two thermometers were made at one minute intervals.

It will be seen from Table I that the Thiele tube, although it showed a much slower rise in temperature than did the new form, gave differences in the readings of the two thermometers that on the average were more than twice as great as those with the new form.

TABLE I—COMPARISON AT LOW TEMPERATURES

Thiele Tube				New Form of Tube			
Thermometer S ° C.	Thermometer T ° C.	Difference ° C.	Duration of heating Min.	Thermometer S ° C.	Thermometer T ° C.	Difference ° C.	Duration of heating Min.
22.6	24.8	2.2	1	22.6	23.8	1.2	1
22.8	25.0	2.2	2	24.6	26.6	2.0	2
23.0	25.4	2.4	3	26.4	27.6	1.2	3
23.2	26.0	2.8	4	27.4	27.8	0.4	4
23.6	26.2	2.6	5	28.0	28.6	0.6	5
23.8	26.2	2.4	6	29.2	30.8	1.6	6
24.0	26.2	2.2	7	30.6	31.8	1.2	7
24.2	26.4	2.2	8	31.6	32.4	0.8	8
24.4	26.4	2.0	9	32.0	33.0	1.0	9
24.6	26.6	2.0	10	32.8	33.8	1.0	10
24.6	26.8	2.2	11	33.4	34.2	0.8	11
24.8	27.0	2.2	12	33.8	34.6	0.8	12
Total rise of temperature in 12 min.			2.2°	Total rise of temperature in 12 min.			11.2°
Average difference of thermometers			2.29°	Average difference of thermometers			1.05°

With the beginning temperature in the neighborhood of 100°, Table II again shows that when the two tubes are heated in as nearly the same manner as feasible with small gas flames, the Thiele tube shows much slower rise in temperature and nearly nine times as great an average difference between the two thermometers as does the new form of tube.

TABLE II—COMPARISON AT HIGHER TEMPERATURES

Thiele Tube				New Form of Tube			
Thermometer S ° C.	Thermometer T ° C.	Difference ° C.	Duration of heating Min	Thermometer S ° C.	Thermometer T ° C.	Difference ° C.	Duration of heating Min.
98.2	106.2	8.0	1	98.8	100.0	1.2	1
99.0	106.2	7.2	2	102.2	103.8	1.6	2
99.6	107.6	8.0	3	106.0	107.0	1.0	3
100.2	108.4	8.2	4	108.4	109.0	0.6	4
101.2	109.0	7.8	5	111.2	112.2	1.0	5
102.0	110.0	8.0	6	113.8	114.6	0.8	6
102.6	110.6	8.0	7	115.4	115.6	0.2	7
103.0	110.0	7.0	8	117.0	117.6	0.6	8
Total rise of temperature in 8 min.			4.8°	Total rise of temperature in 8 min.			18.2°
Average difference of thermometers			7.77°	Average difference of thermometers			0.87°

Tables I and II show the differences of temperature during the heating of the sulfuric acid in that portion of the acid which surrounds the thermometer bulb and sample tube. As the melting point of the substance is approached, the accuracy of the determination will naturally be greatest if the acid in the wide portion of the tube is of the same temperature throughout. The slower the circulation of the acid, or, in other words, the greater the differences in temperature between the upper and lower portions of acid in the wide part of the tube, the greater will be the probability of error in the result of the determination.

To ascertain the completeness of the equalization of temperature in the two forms of tube when they were held within comparatively narrow ranges, Mr. Gilchrist made the measurements that are given in Table III.

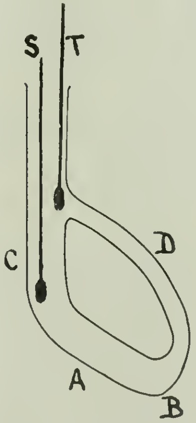

FIG. 1

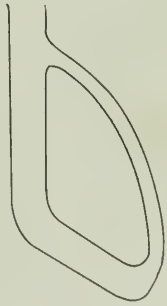

FIG. 2

The form shown in Fig. 1 is entirely satisfactory for student use. However, at the suggestion of Prof. W. R. Orndorff, a tube of the shape shown in Fig. 2 has also been made. In this case the side-arm enters the large tube at a higher point, giving a taller column of sulfuric acid in the main tube. This permits the immersion of an Anschütz thermometer in the sulfuric acid to such a depth that the top of the column of mercury in the thermometer is below the opening from the upper side-arm. The necessity of making correction for a portion of the mercury column above the sulfuric acid is thus obviated. A test of this form of tube has not as yet been made.

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[1] A figure of the Thiele tube is also given in "Analyse und Konstitutionsermittelung organischer Verbindungen," by Hans Meyer, p. 95.

TABLE III—COMPARISON OF UNIFORMITY OF TEMPERATURE

THIELE TUBE				NEW FORM OF TUBE			
THERMOMETER S ° C.	THERMOMETER T ° C.	Difference ° C.	Duration of heating Min.	THERMOMETER S ° C.	THERMOMETER T ° C.	Difference ° C.	Duration of heating Min.
102.6	110.6	8.0	..	132.2	132.8	0.6	..
103.0	110.0	7.0	1	131.8	132.8	1.0	1
102.8	110.2	7.4	2	132.6	131.8	0.8	2
102.8	111.2	8.4	3	131.0	131.4	0.4	3
102.2	110.6	8.4	4	131.4	131.4	0.0	4
102.4	110.4	8.0	5	132.2	132.2	0.0	5
103.0	111.0	8.0	6	132.6	132.8	0.2	6
103.6	111.6	8.0	7	132.6	132.6	0.0	7
104.2	112.8	8.6	8	131.8	131.6	0.2	8
104.4	113.2	8.8	9	131.2	131.2	0.0	9
105.0	113.8	8.8	10	130.8	130.8	0.0	10
105.8	114.4	8.6	11	130.6	130.6	0.0	11
106.0	114.4	8.4	12	130.6	130.6	0.0	12
105.4	113.0	7.6	13	130.8	131.0	0.2	13
103.8	112.0	8.2	14	131.0	131.2	0.2	14
104.2	111.4	7.2	15	131.6	131.6	0.0	15
Maximum change of thermometer S........			3.8°	Maximum change of thermometer S......			2.0°
Maximum change of thermometer T........			4.4°	Maximum change of thermometer T......			2.2°
Average reading of thermometer S........			103.8°	Average reading of thermometer S......			131.55°
Average reading of thermometer T........			111.9°	Average reading of thermometer T......			131.65°
Average difference of thermometers.........			8.1°	Average difference of thermometers.......			0.1°

The determination of melting points with this new form of tube is much more convenient and accurate if the tube is heated electrically rather than by a gas flame. To prepare the tube for electric heating, that portion of the tube marked A (Fig. 1), extending from B to the point where A turns upward, is first covered with a single layer of thin asbestos paper, and then wound with about ten turns of nichrome wire, No. 26, B and S gauge (about 0.016 in. in diam.). The wire is then covered with a layer of asbestos cement to a depth of about 5 mm. These tubes may be made of ordinary soft glass, but Pyrex glass is preferable.

NEW FORMS OF COMBUSTION APPARATUS FOR USE IN GAS ANALYSIS[1]

By **E. R. Weaver and P. G. Ledig**

U. S. BUREAU OF STANDARDS, WASHINGTON, D. C.

Received August 12, 1919

This paper describes two new forms of combustion apparatus for use in gas analysis. The first is an improved form of the Dennis and Hopkins[2] combustion pipette. The second is a combustion capillary of small size somewhat similar to those of Hempel[3] and Levy,[4] containing an electrically heated platinum wire.

COMBUSTION PIPETTE

The combustion apparatus usually known as the Dennis and Hopkins pipette, in which a platinum wire is placed in a pipette of sufficiently large size to hold all the sample to be burned, together with the oxygen necessary to burn it, has been made in many forms. In all of these, however, two leads are brought into the bottom of the pipette, usually through a rubber stopper, and carried through the confining liquid to near the top of the bulb where they connect to the platinum wire. The unsatisfactory features of the apparatus are as follows:

1—It is difficult to make the stopper at the bottom of the pipette and the connections through it perfectly tight. The leakage of mercury is easily detected, but the pipette may be tight to mercury and allow air to leak in when its contents are under reduced pressure, and such a leak is very likely to be overlooked for a long time.

2—The weight of the mercury in such a pipette produces a serious danger of its forcing out the stopper and spilling the mercury.

3—In order to insulate the leads it is necessary to enclose one or both of them in glass tubes. The platinum wire is usually sealed through these tubes and the connection with the lead made inside the glass tube. This is a rather difficult form of construction and one hard to repair. The point at which the wire is sealed through the insulating tube is the most likely to crack in the whole apparatus, and such cracking is very likely to cause an undetected leak. If the leads pass through the glass and the active wire is crimped on, as is sometimes done, the junction usually has the highest resistance of any part of the circuit and is first to fail in use. A solder cannot, of course, be used in the presence of mercury. As the apparatus is frequently constructed, sufficient relative motion between the leads to distort or even break the platinum wire is possible.

4—The necessity of bringing two leads and a tube for the flow of the confining liquid out at the bottom of the pipette makes it difficult to support so heavy a weight without mounting it on a more or less bulky supporting frame.

5—In order to replace the platinum wire it is always necessary to completely drain the pipette and usually to disconnect it entirely.

The pipette shown in Fig. 1 was designed to overcome these difficulties. It is made of Pyrex glass, has a volume of between 125 and 150 cc., and is generally used with mercury as a confining liquid. The two short side-tubes through which the platinum wire is strung are slightly tapered and a cap made of soft glass is fitted to the outside of this taper. A detail of this construction is shown in Fig. 5. Through the end of this cap a heavy platinum wire is sealed. The wire is formed into a loop and the short end also sealed into the glass, as it has been found that this gives much greater strength and lessens the danger of breaking off the wire at the surface of the glass. It is usually best to have the long end of the wire, inside the cap, long enough to go up into the short side-tube at least half a centimeter, since the Khotinsky cement used in fastening on the cap may seal off the inner tube. For the coil which is strung through the pipette, 5 mil (0.125 mm. diameter) platinum wire has been found the best, though this is smaller than is commonly used. It has been found very satisfactory, however, because much less current is required to heat the wire to a dull glow than is necessary with heavier wire, and consequently the whole pipette is not heated to so high a temperature. A finer wire is not stiff enough to hold a good coil. About 7 in. of the wire are wound to a compact spiral on a large needle or heavy wire, leaving an inch or more of straight wire at each end. It is best to use a piece of brass or other stiff wire of small diameter to string this coil through the pipette. The projecting tips of the straight ends of the platinum wire are bent over the edge of the side-tube after the spiral has been pulled tight. The caps are then fastened on the side-tubes with Khotinsky cement, the whole cap and side-tube being gently warmed over the Bunsen burner until the cement flows smoothly in between. When this cools, the Khotinsky holds the wire coil in place and fastens on the cap to make an air-tight joint. When the pipette is filled with mercury, the cups and side-tubes are filled too, and contact is made between the platinum wire in the cup and the heating coil.

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[1] Published by permission of the Director of the Bureau of Standards.

[2] *J. Am. Chem. Soc.*, **21** (1899), 398.

[3] *Z. angew. Chem.*, **25** (1912), 1841.

[4] *J. Soc. Chem. Ind.*, **31** (1912), 1153.

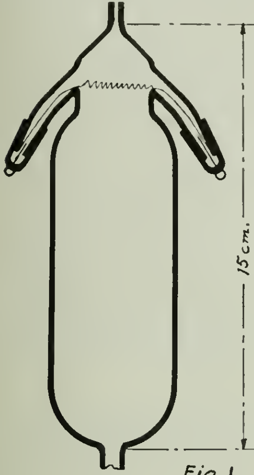

Fig. 1

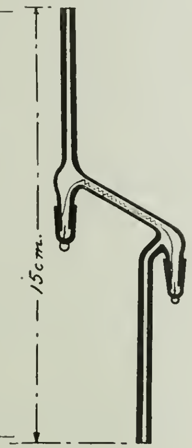

Fig. 2

This pipette gives satisfactory service over a very long period without renewal of the wire if care is used, but if the wire is broken or the coil gets too slack in the pipette, only a few minutes of work are necessary to replace it.

COMBUSTION CAPILLARY

For the determination of small amounts of combustible gas in the presence of air, oxygen, or an inert gas, or for the determination of small amounts of oxygen in a combustible gas, there is a considerable advantage in the use of a combustion capillary similar to that devised by Levy.[1] The tube there described, in which a platinum wire is sealed into a quartz capillary by means of molybdenum leads, is very satisfactory in service; but the coil cannot be replaced if broken or burned out, and the device is expensive and difficult to obtain. A similar capillary devised by Levy, but having the lead wires passing through rubber stoppers, is very unsatisfactory from several standpoints. The capillaries of Hempel[1] and White[2] have objectionable rubber connections between the quartz tube and the glass tubes which carry the lead wires. The Hempel apparatus, at least, is also hard to put together in good form, and must be rebuilt when either the wire or the rubber tubing requires replacement.

The three forms of combustion capillary described below are made of Pyrex glass. They are of a new type which has the following advantages:

1—The wire is easily replaced without disturbing the tube which may be permanently connected to the remainder of the gas analysis apparatus.

2—There are no rubber connections near the hot wire.

3—The tube is easy to make and to keep gas-tight.

4—It is not very difficult for an amateur glass blower to make and should be quite inexpensive if made commercially.

The simplest form is that shown in Fig. 2. The portion containing the coil has an inside diameter of about 3 mm. and the connecting capillary tubing has an inside diameter of about 1 mm. The platinum wire is made into a coil and drawn into place by the use of another wire, as in the case of the pipette previously described. The caps are made of soft glass exactly like those for the pipette and are fastened on with Khotinsky cement. The cap and side-tube are then partly filled with mercury to make electrical contact. Water or mercury may be used as the confining liquid, but mercury has a tendency to foul the tube with oxide in the course of several analyses.

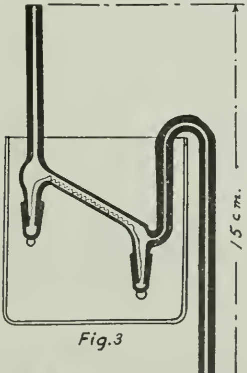

Fig. 3

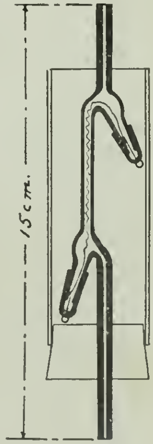

Fig. 4

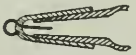

Fig. 5

When water is used as the confining liquid, it is b not to fill the side-tube completely with mercury on account of this oxidation. The bulb-like enlargement is made in the side-tubes to prevent the trapping of gas when the system is filled with water after an analysis, during which some of the water has evaporated from the side-tubes. In use, a double Hempel bulb or similar arrangement is connected to the lower end of the tube to confine the gas as it is passed back and forth.

The first form has proved satisfactory if carefully used, but if water is passed into it while it is hot from a combustion, it is likely to crack. Moreover methane combustions, which require a very hot wire, have in one or two cases so softened the tube that it was bent and the platinum wire fused to the glass. This difficulty can be overcome by making the tube of quartz, but the advantages of using Pyrex glass are such that two other forms were developed in which the tube is kept immersed in a water bath.

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[1] *Loc. cit.*

[2] "Gas and Fuel Analysis," p. 49, McGraw-Hill, New York, 1913.

Fig. 3 shows the first form. It is made exactly the same as that shown in Fig. 2 except that the lower capillary tube is sealed to the side of the lower side-tube and is made with a goose-neck curve which allows a beaker or similar water bath to be slipped up over the tube from beneath. If distilled water is used in this bath, no trouble is experienced from electrolysis between the lead wires. The only objection to this form of tube, of which two have given satisfactory service over a period of several months, is that its awkward shape makes it fragile.

Consequently the third form shown in Fig. 4 was developed. It requires care in making to prevent the gas being trapped in the bends of the main tube when refilling after a combustion. It is also somewhat more difficult to insert the platinum coil, usually requiring a wire hook to catch the end of the stringing wire and draw it around the sharp bend at the upper end, but when it is once made and set up in the water bath, as shown by the light lines in the figure, it gives complete satisfaction.

ADDRESSES AND CONTRIBUTED ARTICLES

THE FUTURE OF INDUSTRIAL ALCOHOLS[1]

By B. R. Tunison

U. S. Industrial Alcohol Co., 27 William St., New York, N. Y.

INTRODUCTION

To attempt to predict the future of industrial alcohol is similar in many respects to making an attempt to foretell the outcome of a battle in a great war. The phases of the question are so numerous and complex and there are so many interdependent influences involved that any one would presume a great deal who attempted to predict with any degree of definiteness the future of industrial alcohol. However, if present influences are considered, it is possible to anticipate at least a few of the more important developments more or less accurately.

IMPORTANCE OF ALCOHOL INDUSTRIALLY

The following statement made by a joint select committee of Cougress in its official report is fully as true to-day as it was the day it was made, some 20 years ago.

> The uses of alcohol other than as a beverage are more largely and widely extended than is generally supposed. But while the use of alcohol as a beverage is purely voluntary its employment for all other purposes is legitimate, beneficial and necessary. No article entering into manufacture or the arts, whether of domestic or foreign production, performs more legitimate or beneficial functions. There is scarcely a manufacturer in the country who does not use alcohol in the production of his goods to a greater or less extent.

Of the various alcohols which have been of industrial importance ethyl alcohol is unquestionably the most important. This alcohol has been subjected to severe trials in the past and burdened by taxes which have caused very great limitations to its legitimate uses. In the industries many costly substitutes have been made because pure ethyl alcohol was obtainable only at prohibitive prices, due to excessive taxes, and because the denatured grades were not suitable for many special purposes.

The importance of methyl alcohol industrially is second only to that of ethyl alcohol. There seems little doubt that this is due to commercial influences rather than to chemical reasons. In the United States it has been substituted for ethyl alcohol for a great many purposes for which it is not so well suited, because of the rules, regulations, and taxes surrounding the manufacture, distribution, and use of ethyl alcohol.

During and since the recent war the demand for methyl alcohol has greatly increased, due in part to the rapidly growing dye industry in this country and also to the enormous export demands because of its limited production in other countries. Its price has more than doubled since the beginning of the war. This increase was not only justified, but necessary, because of the fact that the production of methyl alcohol is limited by the quantity of wood carbonized and because of the low selling price of calcium acetate. It is not likely that this situation will be relieved until such time as methyl alcohol is used only when necessary and not as a substitute for ethyl alcohol in essentially ethyl alcohol processes.

Unless the demand for this alcohol greatly exceeds all present expectations, the standard destructive distillation method for the production of methyl alcohol will probably be used indefinitely. Modifications are being made from time to time, but the basic process is the same and needs no particular discussion at this time.

The future development of the methyl alcohol industry in this country should be very rapid. As the chemical industries are progressing so rapidly, greater and greater quantities of this very essential alcohol will be used. If, as is hoped and expected, the United States becomes one of the largest exporters of dyes, chemicals, and allied products, the use of methyl alcohol will constantly increase. New uses will undoubtedly develop and as these new uses and new industries are expanded methyl alcohol will be of ever-increasing importance in this country.

While many other alcohols are of commercial significance in the United States, their production to any extent in this country has been very recent. Up to the time of the World war it was possible to import an adequate supply. During the war many substances in the production of which the higher alcohols are necessary could not be imported and the importation of the alcohols was almost completely cut off. This had the effect of greatly stimulating the production of these alcohols in the United States. Up to this time large quantities were discarded by many manufacturers because they were in admixture with other bulky waste materials, and their separation more or less difficult. Some manufacturers sold for solvent purposes mixtures of these alcohols, because they could not make the separation and compete with the alcohols brought into the United States from foreign parts.

The production, separation, and purification of higher alcohols is one of the new and rapidly growing industries of this country and should be supported by all users of these products to the greatest possible extent. It is hoped that this industry may survive any periods of depression that may be encountered and that the United States may be independent of any importation of these valuable and necessary alcohols.

The question of the production of ethyl alcohol is so important that it warrants our brief consideration at this time.

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[1] Read before the New York Section of the American Chemical Society, Chemists' Club, New York, N. Y., October 10, 1919.

PRODUCTION OF ETHYL ALCOHOL

RAW MATERIAL—The considerations which have determined the raw materials to be used in the manufacture of ethyl alcohol have been of a commercial nature rather than essentially chemical. At the present time the state of the art is such that from a chemical standpoint alcohol may be readily produced from nearly any available source of saccharine or starchy materials. To indicate the influence of local commercial conditions on the choice of a raw material a few examples may not be out of place.

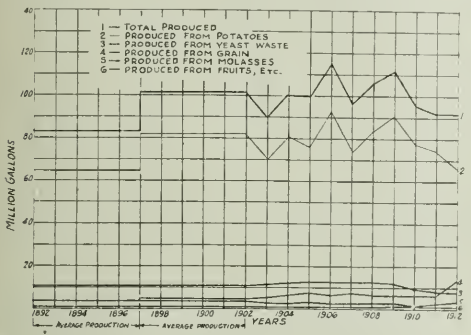

FIG. 1—PRODUCTION OF INDUSTRIAL ETHYL ALCOHOL IN GERMANY, 1892–1912

In Germany—The production of industrial alcohol in Germany has been a noteworthy example of the industry for some years. The production from the various raw materials is indicated in Table I and Fig. 1.

TABLE I—PRODUCTION OF ALCOHOL IN GERMANY (U. S. GALLONS)

YEARS	Potato Distilleries	Yeast Distilleries	Grain Distilleries	Molasses Distilleries	Fruit and Other Distilleries
1887/88–1891/92	59,826,000	10,190,000	3,065,000	3,330,000	686,000
1892/93–1896/97	63,362,000	10,370,000	3,615,000	3,620,000	898,000
1897/98–1901/02	81,730,000	10,900,000	4,750,000	3,190,000	872,000
1902/03	70,000,000	11,500,000	4,990,000	2,350,000	502,000
1903/04	80,420,000	12,060,000	6,204,000	4,410,000	608,000
1904/05	75,900,000	12,720,000	7,500,000	285,000	976,000
1905/06	92,820,000	12,670,000	7,000,000	219,000	819,000
1906/07	73,620,000	12,540,000	7,240,000	235,000	792,000
1907/08	83,100,000	12,770,000	6,440,000	272,000	1,005,000
1908/09	90,220,000	11,900,000	6,310,000	229,000	1,267,000
1909/10	77,600,000	9,460,000	6,150,000	1,936,000	1,005,000
1910/11	74,100,000	8,130,000	6,230,000	2,350,000	739,000
1911/12	66,000,000	7,925,000	13,100,000	3,380,000	898,000

Agricultural and labor conditions during the period indicated were such that potatoes were very cheaply produced and the saccharine material obtained therefrom on a per pound basis was relatively cheap, as compared, for example, with grains. Fruits had a higher value as food and the fruit wastes did not occur in sufficient quantities to materially affect the alcohol production. The molasses available in Germany was largely beet molasses and had a somewhat greater value as a feeding material than as a raw material for alcohol production.

In France—In France sugar beets and beet molasses have been used to a considerable extent as a raw material for production of alcohol. The production from the raw materials used is shown in Table II and Fig. 2.

TABLE II—PRODUCTION OF ALCOHOL IN FRANCE (U. S. GALLONS)

	RAW MATERIAL				
YEAR	Grain Distilleries	Molasses Distilleries	Beet Distilleries	Total	Per cent of Total Production in France
1908	9,560,000	12,620,000	33,300,000	55,500,000	81.5
1909	9,420,000	12,600,000	20,960,000	52,800,000	82.7
1910	12,200,000	13,350,000	31,200,000	56,800,000	90.0
1911	17,450,000	13,300,000	27,800,000	57,600,000	90.0
1912	23,300,000	12,300,000	42,800,000	78,400,000	89.3
1913	11,340,000	16,000,000	41,200,000	68,600,000	88.0
1914	21,700,000	9,940,000	12,370,000	35,700,000	81.5
1915	9,400,000	6,980,000	21,100,000	38,800,000	74.0
1916	17,560,000	4,100,000	11,900,000	33,600,000	81.6

In Switzerland—Consul W. P. Kent of Berne, Switzerland, has stated[1] that calcium carbide is being developed in Switzerland as a source of alcohol. He stated that installations were started with about 20,000 horse power minimum and 30,000 horse power maximum (summer time), which would produce from 7,500 to 10,000 tons of alcohol per annum. Calcium carbide is produced by the usual electric furnace method and acetylene from the calcium carbide by the action of water. Two methods are used in the production of alcohol from the acetylene:

1—Acetylene is hydrogenated by catalytic means and ethylene is produced. The ethylene is dissolved in sulfuric acid, and alcohol and sulfuric acid are formed upon saponification.

2—Acetaldehyde is produced catalytically from the acetylene. The acetaldehyde is oxidized to acetic acid or reduced to alcohol, by means of catalyzers. Great care is used in the selection of a catalyzer in order to eliminate numerous complicated side reactions which are liable to occur.

The production of alcohol by such processes as just described of course necessitates a very cheap source of power. This is available only in such places as Switzerland and Norway, and alcohol made by this means could not compete with alcohol of vegetable origin if such could be produced cheaply in those countries.

In the United States—In the United States many different materials are used with more or less success. In some portions of the country corn and corn wastes are effectively and economically utilized. These products afford a convenient and easily handled source of alcohol. For many years maize was the chief source of industrial alcohol in the United States, and undoubtedly corn and maize will continue to be a very important source.

Alcohol is being made from waste sulfite liquor in some localities where this waste is obtainable in quantity. Up until the present time the production has not been large enough to materially influence the alcohol market. This is largely due to the fact that there are very few places in the United States where sufficient waste liquor can be obtained to produce more than a few hundred gallons of alcohol per day.

So far as the writer is aware there are but two plants in operation in the United States producing alcohol from sawdust, and these have a relatively small production. There seem to be possibilities in the development of the production of alcohol from wood and wood waste.

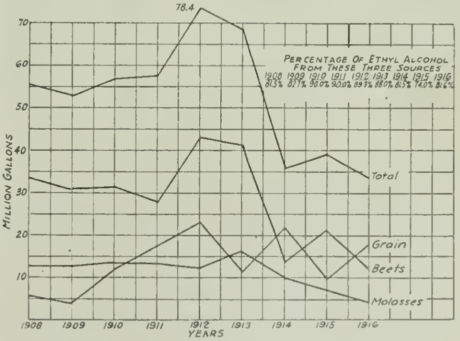

FIG. 2—PRODUCTION OF ETHYL ALCOHOL IN FRANCE

During the last two years very little alcohol has been produced from the various grains. This is largely due to the fact that the grains are in demand as food materials at a high figure. In this country the only time it is feasible to use grains for the

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[1] *Commerce Reports*, **102** (1917), 426.

Table III—Raw Materials for Production of Alcohol in the United States

States and Territories	Raw Materials Corn Bu.	Rye Bu.	Malt Bu.	Other Materials Bu.	Molasses Gal.	D. S. L. Gal.	Total Bu.	Gal.
California	1,656	...	...	...	13,223,826	...	1,656	13,223,826
Connecticut	1,767	1,622	1,311	...	...	...	4,700	...
District of Columbia	79,309	...	122,013	69,909	236,433	...	271,231	236,433
Hawaii	....	...	...	...	7,700	...	....	7,700
Illinois	8,130,912	29,770	880,135	44,993	4,219,519	...	9,085,810	4,219,519
Indiana	2,637,875	48,036	206,883	50,942	...	...	2,943,736	...
Kentucky	2,200,183	87,771	282,019	36	226,980	...	2,570,009	226,980
Louisiana	9,594	132	1,000	2,986	33,214,705	17,620,539	13,712	50,835,244
Maryland	130,522	2,734	5,176	...	34,626,539	...	138,432	34,626,539
Massachusetts	2,690	2,418	1,272	...	13,118,139	...	6,380	13,118,139
Michigan	....	...	...	...	...	5,290,164	....	5,290,164
Missouri	13,967	1,986	2,444	...	...	...	18,397	...
Montana	....	...	...	...	249,340	...	....	245.340
New York	342,150	37,712	69,158	...	11,025,740	28,637,832	449,020	39,663,572
Ohio	578,451	3,170	63,324	784	...	...	645,729	...
Pennsylvania	295,793	7,116	33,213	...	7,873,097	...	363,122	7,873,097
Rhode Island	....	...	...	7	5,942	...	7	5,942
South Carolina	....	...	...	2,382	...	16,958,609	2,382	16,958,609
Texas	....	...	...	...	...	20,098	....	20,098
Wisconsin	119,676	26,397	21,729	...	...	...	167,802	...
Total	14,544,545	248,864	1,689,677	172,039	118,027,960	68,527,242	16,665,124	186,555,202
Total for Fiscal Year 1917	33,973,268	3,375,439	4,239,677	81,435	112,497,633	78,462,969	40,669,819	190,960.602

production of industrial alcohol is when a crop has been damaged in some manner so that it cannot be utilized as a food material.

Labor and agricultural conditions have been and are such in this country that potatoes cannot be grown economically enough to compete with trade wastes as sources of alcohol.

Fruit in this country is so valuable as food that it cannot be used as a source of industrial alcohol. Fruit wastes do not occur in sufficient quantity to supply even a centrally located distillery and transportation of such products is of course not feasible.

Table IV—Production of Alcohol in the United States

States and Territories	1918 From Materials other than Fruit Gal.	Fruit Brandy Gal.	Total Production Gal.	1917 Total Production Gal.
California	8,727,694	5,295,952	14,023,646	17,851,482
Connecticut	23,527	2,924	26,451	132,055
District of Columbia	749,517	.....	749,517	608,812
Hawaii	3,935	.....	3,935	14,016
Illinois	49,679,940	140	49,680,080	79,320,617
Indiana	15,820,031	10,899	15,830,930	43,361,276
Kentucky	12,604,703	3,734	12,608,437	36,441,778
Louisiana	24,406,539	.....	24,406,539	26,545,832
Maryland	26,746,386	.....	26,746,386	24,965,321
Massachusetts	10,873,375	.....	10,873,375	12,511,238
Michigan	752,745	.....	752,745	819,908
Missouri	77,026	2,501	79,527	289,661
Montana	186,248	.....	186,248	244,773
Nebraska	.....	.....	.....	2,938,594
New Jersey	.....	51	51	54,494
New Mexico	.....	.....	.....	315
New York	10,540,421	4,480	10,544,901	13,856,054
Ohio	3,277,485	36,618	3,314,103	10,114,573
Pennsylvania	7,293,914	.....	7,293,914	12,190,764
Rhode Island	2,845	.....	2,845	224
South Carolina	943,568	.....	943,568	1,159,309
Texas	7,281	.....	7,281	13,905
Virginia	.....	.....	.....	122,957
Wisconsin	759,294	.....	759,294	2,527,249
Wyoming	.....	26	26	260
Total	173,476,474	5,357,325	178,833,799	286,085,464

Summary

	Gal.
1913	193,606,258
1914	181,919,542
1915	140,656,103
1916	253,283,273

Sugar beets and beet molasses have not been used to any extent for the production of industrial alcohol in this country, because at present they are utilized for feeding purposes and they cannot compete with other trade wastes.

The chief source of industrial alcohol in the United States is cane, or black strap, molasses. Only a few years ago, especially in the East and West Indies, the disposal of molasses by the sugar mills was a serious trade waste problem, but it is now very largely used the world over as a raw material for alcohol manufacture. The conversion of molasses into alcoholic liquor, especially into rum, is an old enterprise. West India rum has been famous in New England for more than 200 years. But the use of molasses in large quantities for industrial alcohol production is a development of the last few years. As far as ease of manipulation is concerned, molasses unquestionably surpasses any other known material. Moreover in the past it has been a very cheap material. A large portion of the world's molasses is still a waste product due to the difficulty and expense of transportation to the commercial centers.

Molasses from Cuba and Porto Rico is of special importance to the United States, because of the several million tons which are annually available for the production of alcohol. This molasses is gathered from the various producing mills in barges, steam lighters, hundreds of tank cars, and in some few cases barrels and hogsheads, and taken to the large storage tanks which are located at deep water shipping ports. Tank steamers, such as are used for the transportation of petroleum, are used to carry the molasses from these storage points to various plants in the United States: in Boston, New York, Baltimore, New Orleans, and other points. In addition to the abovementioned sources of molasses large quantities are obtained from the cane sugar refineries located in the southern and southeastern parts of the United States.

The various raw materials used and the quantities of alcohol obtained from them are indicated in Tables III and IV.

The figures are, of course, totals and include the beverage alcohol production.

The total production of ethyl alcohol in various countries from 1908 to 1912 is shown graphically in Fig. 3.

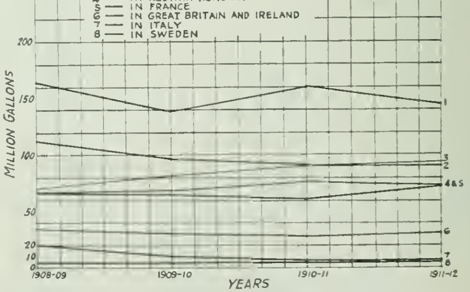

Fig 3—Production of Ethyl Alcohol, 1908–1912

PRODUCTION OF DENATURED ALCOHOL

In the last few years the production and consumption of denatured alcohol in the United States has increased very greatly, as shown by Table V and Fig. 4.

TABLE V—PRODUCTION OF DENATURED ALCOHOL IN THE UNITED STATES

Fiscal Yrs.	Denaturing Warehouses	Completely Denatured Wine Gal.	Specially Denatured Wine Gal.	Total Wine Gal.	Total Proof Gal.
1907	8	1,397,861	382,415	1,780,276	3,084,950
1908	12	1,812,122	1,509,329	3,321,451	5,640,331
1909	12	2,370,839	2,185,579	4,556,418	7,967,736
1910	12	3,076,924	3,002,102	6,079,027	10,605,870
1911	14	3,374,019	3,507,109	6,881,129	11,682,887
1912	14	4,161,268	3,933,246	8,094,515	13,955,903
1913	21	5,233,240	4,608,417	9,831,658	16,953,552
1914	25	5,213,129	5,191,846	10,404,975	17,811,078
1915	23	5,386,646	8,599,821	13,986,468	25,411,718
1916	33	7,871,952	38,807,153	46,679,108	84,532,253
1917	44	10,508,919	45,170,678	55,679,597	93,762,422
1918	49	10,328,454	39,834,561	50,163,016	90,644,722

The falling off in the quantity of denatured alcohol used during 1918 is accounted for by the fact that in the early part of the year several of the larger munition plants discontinued the manufacture of explosives for the Allies in which denatured alcohol had been used, and engaged in the manufacture of explosives for the United States Government, using principally tax-free undenatured alcohol. The army specifications were subsequently changed and denatured alcohol was used exclusively in those plants. The quantity of denatured alcohol used during the year in the manufacture of explosives and for other war purposes was approximately 52,847,117 proof gallons.

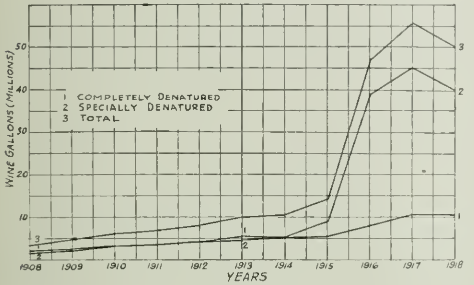

FIG. 4—PRODUCTION OF DENATURED ALCOHOL IN THE UNITED STATES

NEW SOURCES OF RAW MATERIALS

Upon the demand for alcohol and the price at which it is sold will depend the new raw materials used for its production. Of the possible raw materials which have been proposed may be mentioned the following:

ARTICHOKE—The tubers of the artichoke contain on an average about 14 to 15 per cent of directly fermentable levulose and about 2 per cent of starch which can be converted into sugar. It is possible that these tubers may be used to some extent where they may be easily grown.

SORGHUM—This plant contains from 6 to 15 per cent of levulose and crystallizable sugar. It deserves considerable attention because of the readiness with which it is grown, the extent of the territory in which it flourishes, and the large amount of sugar which certain varieties contain.

FRUITS AND FRUIT WASTES—Fruits and fruit wastes may be used for the production of alcohol, but in most cases the fruits are too valuable to use for such purposes and the wastes do not occur in quantities sufficient to maintain a distillery. Transportation of these wastes is not possible.

BERRIES—While many different berries have been used for the production of alcoholic beverages, in most cases it will not be possible to use them for the production of industrial alcohol, because of their greater value as food.

AGAVE AND CACTUS—While various specimens of the agave and cactus have been used in Mexico and the southwestern parts of the United States for the production of alcoholic beverages, they have not been used as a source of industrial alcohol. It is known that the juice of these plants contains large amounts of sugar at times and there is reason to believe that they may be used industrially. Recently some experimental work has been done on the so-called "Sotol" plant of Mexico, with promising results. It is possible that these plants may be used to some extent for the production of industrial alcohol.

CASSAVA—The root of the cassava contains about 25 per cent of starch which may be utilized for the production of alcohol. A few years ago the Bureau of Chemistry determined that an average of 40 gal. of alcohol per ton of roots could be obtained. If these roots can be cheaply grown this is a promising possibility.

GARBAGE WASTE—This material has been suggested as a source of industrial alcohol. That this cannot be a factor in the production of industrial alcohol we can readily see when we consider that the material is poor in fermentable substance and would be very expensive to handle.

PRODUCTS OF COAL DISTILLATION—The report of the British Inter-Departmental Committee on the Production and Utilization of "Power Alcohol" states that sufficient ethylene can be obtained from the gas works and coke-oven gases of Great Britain to yield annually up to 150,000,000 gal. of 90 per cent alcohol. It is believed that steps are being taken to utilize these wastes which may become important.

In other countries there are many raw materials not yet used extensively which will probably become important sources of industrial alcohol. In tropical regions there are large numbers of plants from which alcohol can be readily produced. As an example may be mentioned the Nipa palm which flourishes in the Far East, India, Africa, etc. Concerning the utilization of this plant for the production of alcohol, the following statement has been made:[1] "There are over 100,000 acres of Nipa swamp now available in the Archipelago (Philippines) of which about 90 per cent have never been touched, and it is estimated that the untapped swamp area of the islands would yield 50 million gallons of alcohol every season."

In addition to the requirement of a sufficient percentage of fermentable matter to give a yield which will pay for the handling, etc., of the latter, there must also be an abundant, concentrated, and stable supply of raw material. Few people realize that a small alcohol plant of even 100 gal. daily capacity will consume every day approximately 200 gal. of molasses, or one ton of shelled corn, or 4 tons of potatoes (about 15 per cent starch), or 7 to 8 tons of sweet apples (about 12 per cent sugar). A concentrated supply must be available because otherwise labor and transportation charges become prohibitive. The supply must be constant as it does not pay to run an alcohol plant only at intervals. This is an important factor when considering fruit, corn, or other wastes. Questions of whether the material will stand transportation and storage are often determining factors.

The raw material for the future production of industrial alcohol then will be determined largely by economic and local conditions. In this country, as conditions are modified, possibly many new materials may be used for this purpose, depending upon these conditions. For some time to come, however, in this country molasses will probably be the most important raw material for the production of industrial alcohol.

MANUFACTURE FROM RAW MATERIALS

The alcohol industry as it stands to-day is the result of a very long period of development. The methods and apparatus used have become pretty well standardized and no revolutionary changes or developments are anticipated. Many minor improvements are being made from time to time, but as far as the distillation and rectification are concerned the principles involved have been carefully worked out and apparatus designed which correctly applies them.

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[1] *Pure Products*, **14** (1918), 286.

A large amount of research is being directed towards the processes of fermentation and we may hope for many developments from this phase of the industry. Paralleling this development, better systems of plant control will undoubtedly be put into practice. While the yields obtained at present are good, better results are being searched for.

USES OF INDUSTRIAL ALCOHOL

As far as the influence of the industries in which alcohol is used is concerned, the use of alcohol in the future should develop fully as rapidly as the industries themselves. If this were the only, or even the most important factor, as it is concerning most commodities, the prediction of the future would be a relatively simple matter. Most of the newly developed chemical industries in this country have come to stay and they will require an ever-increasing quantity of alcohol.

While most of the uses of alcohol will be developed more or less parallel with the development of the chemical and allied industries, there are a few the expansion of which will be more or less revolutionary in character.

SOLIDIFIED ALCOHOL—One of the very important uses to-day, and one that is becoming increasingly so, is that of solidified alcohol. Alcohol burns with a smokeless flame and does not carbonize like kerosene, so that even at the present time it is a very satisfactory fuel, and its only rival for chafing dishes, coffee percolators and such articles is electricity. In regions where electricity is not available solidified alcohol is a very important fuel for cooking purposes. It is also used very extensively during vacation trips to the mountains, or the seashore. It is very convenient to handle and is without dirt, smoke, or odor, and is an economical fuel, and undoubtedly the use of alcohol in this form will increase to a very marked degree.

PURIFICATION OF TURPENTINE—One of the newer developments is the utilization of alcohol in the separation and purification of gum-turpentine. The present method of heating and making the crude products at the turpentine camps results in rosin of which only a small part is of good color. It has been found that the crude gum-turpentine is readily soluble in high proof denatured alcohol. It is then possible to remove such foreign matter as particles of wood, twigs, insects, etc., which have been found largely responsible for coloring the finished products. Subsequent distillation of the gum-turpentine-alcohol solution results in a separation of the alcohol heads containing a small percentage of turpentine, which functions as a denaturant and at the same time produces a product which can be used again as a solvent. The turpentine fraction is clear and marketable as a high-grade product and the rosin residue is colorless and of the highest grade. The loss of solvent at present is approximately 6 per cent and developments indicate that it may become lower. When using this process it is possible to centralize the processing of the gum-turpentine and thus reduce operating expense to a minimum. The increase in quantity of high-grade products, the very small losses involved, and the small cost of operation incurred by this process indicate that it will become of very great importance in the turpentine industry.

ETHYLENE—Another relatively new development in the utilization of alcohol is in the catalytic production of ethylene. Ethylene has been considered as a substitute for a cutting and welding gas in the place of acetylene. From comparative tests ethylene is found to have many advantages over acetylene. As far as the heat of combustion is concerned ethylene has a slightly higher value. In cutting and welding iron and steel ethylene has among others the following advantages:

1—It has a high ratio of carbon to deterrent element like hydrogen, overcoming the tendency to retard combustion and slow the cutting.

2—It has a rapid rate of combustion, preventing loss of temperature from absorption and conduction of heat by the metal being cut.

3—It will help to maintain an oxidizing effect fast enough to overcome any tendency to burn too deeply or chill the surfaces of the metal being cut.

4—It will produce a rapid rate of cutting with a low consumption of gas making a high efficiency possible from the regular operators of the torch.

5—It shows a decrease of labor and gas consumption with increase of thickness of metal cut, making the cutting of thick metal as economical as thin metal.

6—It possesses a remarkable degree of lightness of the charged cylinders, providing a valuable portability and ease of movement of the gas supply about a shop.

7—It is a non-poisonous, safe gas, without objectionable odor.

8—It has a clearly outlined cone in the flame, without which a workman would be badly handicapped.

In the working of copper it has been impossible to make a satisfactory weld with acetylene, because of the formation of carbon and the consequent blistering in the weld. Perfect copper welds have been obtained with ethylene.

In aluminum welding and lead burning ethylene is infinitely better than acetylene. There is no carbon formation and no kick back in the burner while a terrific heat may be maintained.

It is a much safer gas to handle since it does not explode spontaneously. It can be compressed and handled in the standard form of gas cylinder without either packing or a solvent (acetone). For this reason it is possible to make a saving of about one-half in the cost of the cylinders and approximately one-half in the freight cost. Furthermore, ethylene can be compressed so that a cylinder will hold over 200 cu. ft. of ethylene. Thus the cost per cu. ft. for shipment is again cut in half. Ethylene is essentially a "one man" gas. The weight of ethylene per 100 cu. ft., including the container, is only 40 lbs. as compared to 90 lbs. for acetylene. A cylinder of ethylene weighing between 80 and 85 lbs. contains approximately 210 cu. ft. of gas and can be easily handled by one man.

Ethylene is being sold at the same price as acetylene. It may be used in an ordinary welding torch, but preferably one with a mixing chamber. A change in the size of the tip is also desirable.

In addition to the use of ethylene as a cutting and welding gas it has been found to have considerable value for lighting and heating purposes where electricity is not available.

In the chemical industries we all realize that with a source of cheap, pure ethylene it will be possible to manufacture a great number of synthetic and chemical products.

INTERNAL COMBUSTION ENGINES—Probably the use of alcohol which in the future will have the greatest significance is its use as such, or in admixture with other compounds, as a fuel for internal combustion engines. For years volumes have been written about the use of alcohol in such engines. In Germany where the supply of petroleum products was inadequate and where alcohol was a relatively cheap commodity, large quantities were used for automotive and power purposes. In France alcohol was used extensively for automotive engines. In the United States considerable has been said about using alcohol for automobiles, farm machinery, etc. Vivid word pictures have been drawn of the farmers taking their waste products and processing them in their small plants and then doing everything from sawing wood to doing the family washing with alcohol as a source of power. However, the petroleum supplies in this country have been so abundant and available at such reasonable prices that these word pictures have remained as such and the farmers continue to buy gasoline with which to operate their automobiles and small engines. This has been the case since the agitation for alcohol production by the farmers in 1906–7.

Recently, however, conditions have suddenly changed. The Geological Survey tells us that in about 3 years the peak in a curve showing petroleum production will be reached and after that time there will be a gradual decline in petroleum production over a long period of years.

Not only will the production of petroleum continually decrease, but the present indications are that the demand for petroleum products will increase in the next few years even more rapidly than ever. The increase in the number of automobiles, trucks, tractors, and airplanes during the last 5 years has been remarkable. If the increase from now on is only a small percentage of what it has been we must soon obtain a new supply of explosion engine fuel, and while our supply of petroleum is limited in quantity, the raw materials for the production of alcohol are around about us in inexhaustible quantities. At this time the utilization of alcohol for power purposes appears very significant.

While it will probably be several years before alcohol alone will be used as a motor fuel, alcohol in admixture with other fuels is now being produced and marketed in some localities of this country. The alcohol fuels as used at present do not require a specially designed engine to obtain optimum results, but the standard engine and accessories are used with excellent results. Alcohol fuels have many advantages over gasoline when used in automotive engines, some of which may be summarized as follows:

Greater mileage
No preignition
No knocking
More uniform application of power during power stroke of the piston
More power
Power more completely under control

Even though the alcohol has a lower B. t. u. value for the heat of combustion, the combustion of the fuel is more complete and greater efficiencies are obtained. This is especially true in slow speed engines such as motor trucks.

Alcohol fuels have also been developed for airplane use. In this regard the *Journal of the Society of Automotive Engineers*[1] says in part:

> A new alcoholic fuel, consisting of alcohol, benzol, and ether, is about to take the place of the high-grade airplane gasoline, which has previously been used in the Air Mail Service.
>
> The advantage of this fuel lies in the resulting cleanliness of the engines, reduction in the cost of upkeep and its burning cooler than gasoline, which to some extent overcomes the objection to a high-compression engine when operating at low altitudes. It requires about four-fifths as much of the new fuel for any given distance and altitude. This gives greater flying radius to the planes and will enable the DeHaviland Fours to cover the New York to Cleveland route, a distance of 430 miles, in a non-stop flight. It reduces the probability of forced landings by keeping the spark plugs and the engine cylinders clear of carbon deposits and accumulations of oil.

As the realization of the advantages of the above-mentioned fuels becomes more universal, and as the quality of the gasoline becomes poorer due to the diminishing petroleum supply, and as the price of gasoline rises, alcohol will be used in greater and greater quantities. In anticipation of this great increase in the demand for alcohol for power purposes we should take active steps to assist in the development of the alcohol industry so that an adequate supply of alcohol may be at hand when needed.

PROBABLE EFFECT OF LEGISLATION ON THE FUTURE OF INDUSTRIAL ALCOHOL

The effect of the passage of the industrial alcohol bill in 1906 had a marked effect on American industries in which alcohol is used. Many new enterprises were undertaken and those in operation were greatly extended. Since 1907 these industries using alcohol have prospered and grown until the United States instead of being one of the smallest nations from an industrial alcohol point of view has now become one of the greatest world influences. The increase in the production of industrial alcohol since 1907 is summarized in the last two columns of Table V.

While the progress made by the alcohol industry has been little short of remarkable, our chemical industries which depend very largely on a supply of cheap alcohol have not prospered as have those in some other countries. The bill of 1906 was an important step forward, but the manufacture, sale, distribution, and use of alcohol was so surrounded with rules and regulations that many manufacturers did not use it and the normal growth of the industry was never approximated.

When the present prohibition bill was being discussed and prepared the very existence of the industries using industrial alcohol was threatened. The Commissioner of Internal Revenue with very great foresight and with a realization of the necessity of a supply of alcohol for industrial purposes, the use of which should be as free of restrictions as possible, prepared and presented the section of the prohibition bill relating to industrial alcohol. The assistance given by the Internal Revenue Bureau in showing the necessity of industrial alcohol, and the absolute dependence of some industries on a supply of alcohol, to those concerned with the making of our laws was a coöperation with the chemical and allied industries which should be known and appreciated by every chemist. A great deal of credit should be given to members of the present Congress who took time to learn facts concerning some of the industrial phases of the alcohol question, with the result that the industrial alcohol section of the bill was passed.

Now that a new law is to govern the alcohol industry we may feel certain that the Internal Revenue Bureau will proceed in the same just manner in drafting the rules and regulations which are to surround the manufacture, sale, distribution, and use of alcohol. We may feel confident that the Government's taxable interests will be protected and at the same time the manufacturers will be given the greatest possible freedom in the use of alcohol for industrial purposes. Due to the attitude of fairness of the Internal Revenue Bureau it is not too much to expect that we shall have alcohol under such conditions as will be an added stimulus to the progress of our rapidly growing chemical industries.

Aside from the natural growth of the alcohol industry care should be taken to foster its development. We are told that we should maintain a policy of preparedness throughout the coming years. Now that the whiskey distillery is to be a thing of the past where could we look for a supply of alcohol in case of war? In the recent war the distilleries came to the rescue and in case of another war we must have industrial alcohol plants in operation which could immediately supply large quantities of a most necessary product.

It has been said that the future increased production of alcohol could be attained by persuading the farmers to produce alcohol in small agricultural distilleries in a manner similar to those in operation in Germany. There are several reasons why this is not likely to take place. Labor is very much higher in this country than in Germany. The farmers of this country have become accustomed to production on an extensive scale rather than in an intensive manner, and are not likely to be satisfied with the results of a small distillery. In order to obtain satisfactory results the fermentation must be carefully controlled and the average farmer does not possess sufficient technical training to do this effectively. The manipulation of an alcohol plant is difficult except to the technical man. These farm installations would necessarily be small units because of the limited quantity of raw material available, the cost of the installation would be high, the labor cost would be excessive, the output would be small, and the unit cost of production would be so high that the farmer could buy alcohol cheaper than he could make it. Our case is quite different from that of Germany where these conditions do not exist, and where the industry has been subsidized by the government. Without such subsidy and government pressure it is the writer's opinion that the farmers of this country are not likely to produce alcohol for industrial purposes for some time.

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[1] *J. Soc. Auto. Engrs*, **5** (1919), 207.

Alcohol is essentially a cheap commodity and should be treated as such. To-day this is not the case, and the manufacturer may be partly to blame for this condition. If manufacturers using alcohol in quantity would buy alcohol as they buy other commodities in tank car lots and not require shipment in expensive cooperage or steel drums, they would help to remove the impression that alcohol is such a valuable product. The ordering, billing, shipping, returning, crediting, etc., of these packages is a nuisance as well as a source of considerable expense. Alcohol is the only product in the history of the United States which has been taxed several hundred per cent of its value. This has given the impression that industrial alcohol is also extremely valuable. As the uses of alcohol are developed and as it becomes used more extensively for such purposes as motor fuel, it is not too much to expect that it should be handled in much the same manner as petroleum and its products. Great Britain is beginning to realize that alcohol is essentially a cheap product and should be treated as such. The British Inter-Departmental Committee on the Production and Utilization of "Power Alcohol" recommends in part the following:

> As the price of alcohol for power and traction purposes, to which we propose the name of "power alcohol" should be given, must be such as to enable it to compete with gasoline, it is essential that all restrictions concerning its manufacture, storage, transport, and distribution should be removed so far as possible, consistent with safeguarding the revenue and preventing improper use, and that cheap denaturing should be facilitated.
>
> Finally, we are of opinion that steps to facilitate the production and utilization of power alcohol in the United Kingdom can in no circumstances be taken, nor arrangements for such development carried into effect, unless provisions and alterations of the kind we recommend in our report are made in *advance* of the time when an acute recurrence of high prices for motor fuels may otherwise call for action too late for it to be effective.

Why should not the common carriers in this country as well as our Government recognize that industrial alcohol is a 50 cent commodity and not one of $5.00 value? Why shouldn't manufacturers assist in bringing about such a recognition by using the specially denatured alcohols wherever possible and not be frightened by such words as "permit," "bond," and similar words identified with the Internal Revenue Bureau. The Commissioner of Internal Revenue is the friend of the manufacturer using alcohol and not his enemy. He will endeavor to assist you and not retard your progress. Over 40 formulas of specially denatured alcohol have been authorized for use in the manufacture of over 350 articles in addition to many class authorizations. The Commissioner of Internal Revenue will consider the authorization and the extension of the use of any formula in new industries or will consider the authorization of new formulas, if existing formulas are not applicable. As long as the Government's taxable interests in the alcohol are protected it may be freely used by the industries.

The requirements of the Internal Revenue Bureau surrounding the use of specially denatured alcohol are neither difficult nor prohibitive. The papers may be easily prepared. If you are a user of alcohol why shouldn't you take advantage of your privileges and assist in the stabilization and progress of our American chemical industries?

If the United States builds up a large industrial alcohol production and fosters its growth and development the industries will benefit and there is no question but that this nation as a world power will be stronger. During peace the nation will be strong because of its industries; during war these industries using alcohol will be instantly available as the media for the production of war materials.

CONCLUSIONS

In the preceding paragraphs it has been possible to mention only a few of the probable influences affecting the future of industrial alcohols, and to attempt to indicate in a general manner their effect on the future. Now that the realization of the necessity of industrial alcohol is becoming more general, legislation favorable to manufacturers is taking place and the industries using alcohols are developing rapidly. May we not look forward to the time when the industry of making industrial alcohols in the United States will be of such a magnitude as to be a great national asset under all conditions?

RECONSTRUCTION ASPECTS OF SOME CHEMICAL INDUSTRIES IN THE UNITED STATES[1]

By Edward Gudeman

Chicago, Illinois

It often takes a major operation to save the life of a person or of a nation. The glorious outcome of the war has not alone saved the life of our own people, but has been the salvation of the world, has amputated the heads of autocracy, sounded the death-knell of the cankerous German confederation, and in doing so, has saved the life of the German nation as well.

This heroic military operation brought to life the American chemists, who two years ago were hardly known by name, but who stand to-day before the world, the equal of our fellow-chemists in any of the four quarters of the globe. The horizon is still too near and the time elapsed too short to tell what they have done to help attain a mastery in the air, on the earth's surface, and below its depths, on land and sea. This must be left for coming historians of chemistry. We are now in the critical convalescent after-period of this military operation, and whether we fully recover and become economically, socially, and industrially stronger—in fact whether we survive or not, for the benefit, welfare, and prosperity of ourselves and coming generations—depends on what we do now, on our reconstruction program, its construction and operation. It is not with us a question of readjustment or of rehabilitation or of reclamation, but of reconstruction. Our reconstruction means *construction* of a structure that will justly and fairly meet our present and coming social and industrial problems. It cannot be a plan of one or a few and we cannot expect to erect it within a day or a few weeks. To-day we can only and must lay its foundation stone, anchored firmly on a bedrock of justice and equality.

The statement that "Money wins wars" has been shown to be false. It is loyal man and woman power, abroad and at home, inside and outside of uniforms, to whom the victory must be credited. No class, no profession, no sect can be singled out, and what I claim for our profession, others may claim for theirs.

Chemistry helped to create our powerful navy and our new merchant marine, and we must do our best to see that neither of them remains at a standstill. To-day the United States flag is flying on all the seven seas and never again will leave them, with or without a "Liberty of the Seas" whatever that may be or mean. To-day every land- and water-way is open to us, and must be kept so for us to take our place and have our share in the world's commerce.

Let us see to what extent our war allies of yesterday have become serious trade rivals, or perhaps friendly trade enemies. We all know that at the time of signing the armistice large stores of all kinds were accumulated and isolated in the Southern Hemisphere and in the Far East. Immediately with the release from military duties of a very large number of ocean carriers, these stores became accessible and available, and are now floating back through the old commercial channels into their former markets. Great Britain and France are taking advantage of these national opportunities, perhaps national obligations, and are cutting away from the United States, except so far as pre-war contracts and immediate necessity compel them to still deal with us. Commodities bought by foreign nations, and still in our country, are being resold to us at reduced prices.

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[1] Address before the American Institute of Chemical Engineers, Chicago, Ill., January 15, 1919

Within thirty days of the signing of the armistice, negotiations were completed between Argentina and Great Britain and France for the whole wheat crop of that country, and, to facilitate payment, Argentina is said to have loaned $240,000,000 for two years to England and France. Sugar is on its way to England from Java and Australia. We shall hold the bag for the Cuban crop as we guaranteed a fixed price for it, anticipating that England and France would take not less than 40 per cent thereof. Argentina and Australia are now shipping meats to Great Britain at 6 to 10 cents per pound below our export prices.

Great Britain is an asset to the Southern Hemisphere and the Far East, and the United States a liability. Friendship and commerce mix even though preference is a matter of dollars and cents, of francs, shillings, and marks. Therefore to protect ourselves, whether chemists or not, our reconstruction program must extend beyond the boundaries of our own country and we must make part thereof the underlying principle announced to his country by the British Minister of Reconstruction, that "the problem of reconstruction begins with shipping." Great Britain had a Minister of Reconstruction for many months before the signing of the armistice. What have we done and what should we do? We have appointed uncountable commissions, committees, and federal, state, county, and city trade boards, many unable to see beyond their own local horizon, or their own individual interests, some even tainted with political aspirations.

Anyone, whether chemist or not, can enumerate many problems that our reconstruction program should solve, and I have picked out a few, such as:

1—It is the moral and patriotic duty and obligation of the reconstruction program to put back into industry or commercial life, every soldier and sailor who has in any way become incapacitated, directly or otherwise, due to the war.

2—Our reconstruction program must give protection, assistance, and encouragement to all newly established and all newly developed American industries, many of which, if not directly chemical, have a chemical underlying basis. Of course, those which are exclusively war industries can be ignored.

3—The program must be one which will conserve our natural resources and our raw materials. Finance must come to the assistance of industries, not alone from private sources, but from our Government, through loans, subsidies, and otherwise. We must have protection, perhaps through regulated and controlled federal corporations. Mr. Frank A. Vanderlip stated "we must make great shipments of foodstuffs, of raw materials and in a lesser measure of manufactured products immediately after the war, and they cannot be paid for by equal shipments of goods to this country. Payment must be made to us through bonds and securities." This is very true from the viewpoint of his profession, finance, but it does not go far enough. For the protection of our industries we should be most conservative in the shipment of our raw materials, especially from our natural resources, and more liberal credits should be extended to American manufacturers to enable them to export our manufactured products. We should never again ship our raw materials in carload lots, and take them back in manufactured form, in ounce packages; and be forced, moreover, to compete with them both in foreign markets and at home due to liberal credits even now extended to our war allies and trade rivals.

The rank of a country among the nations is dependent on its ownership, control, and conservation of raw materials. The break through at Chateau Thierry sealed Germany's doom, not because it was a great military victory, but because it drove the opening wedge into Germany's commercial position, driving the Huns from necessary raw materials. Deprived only of two chemical essentials, iron and coal, a new Germany, whatever its geographical and political boundaries may be, will never again be a menace to the world, never again can gain a commercial ascendancy, and will remain a minor power among the nations.

4—Health problems of to-day are distinctly chemical, and must have a strong plank in our reconstruction platform, not alone as to the prevention of disease, but as to protection against disease. We must incorporate therein the problems pertaining to sanitation, housing, vital statistics, birth registration, and many other social health reforms. We must have interstate health regulations as a regular thing, not only as an emergency call. A national health administration should be organized, not on strictly medical lines, but on lines similar to those of our past Food Administration, primarily educational, bringing health teachings into every household.

5—It is an absolute necessity that our reconstruction program include a strong educational policy. We should have compulsory education as a fact, and the education must be in English. We must obtain real Americanization of all our foreign-born citizens, of our immigrants, of our illiterate mountain white population, and of our negroes.

6—Transportation problems must be settled in our reconstruction program, and as all transportation, whether of commodity or speech, depends on fuel or electric power, the chemists are vitally interested in the correct solution of this problem.

7—Economic equality is one of the greatest and most important problems to be considered in our reconstruction program. Chemists are only a small part of the mass that must try to settle the questions as to labor and capital. Women are to-day acting as chemists in many industries, and the records show that as to capability and efficiency they are equal to the men. We are directly involved in the settlement of the replacement of man's labor by woman's labor, and *vice versa*. This great problem of the replacement of the one by the other can only be justly solved through individual selection, based on personal considerations, and it cannot be at the expense of man or woman as a class.

Economic equality is of international scope and will affect political and diplomatic questions, may eliminate reciprocity treaties, and most favored nation acts; will affect taxes and duties, and can regulate immigration and emigration; may bring about an international day of labor, with a minimum wage scale. It is of such magnitude that it can be a consideration of the Treaty of Peace, and may even become the preamble of the Constitution and By-Laws of a coming League of Nations.

Considering some of these reconstruction problems from the narrower viewpoint of the chemical profession, let us see where we stand and what we can do to become a force in solving some of these problems.

Nothing pleases a child more than to be able to say "I told you so," and I admit being childish. At the meeting of the AMERICAN CHEMICAL SOCIETY in April 1914, I asked: "What is the standing of the chemists in the United States, not as we see ourselves but as others see us? In fact do we, as a profession, exist at all? Is it not time (1914) for the chemists to get the recognition due them and to place the profession on the high plane it should occupy? In Illinois the only two scientific professions that can be followed by anyone without a license, permit or qualification to practice, are those of cooks and chemists."[1] To-day we are known and stand on a high plane, but as to qualifications and requirements there has been no change; in fact, many are acting to-day as chemists who hardly know what the word means, and who have had no training at all, not even a diploma from a school of correspondence. We have no legal or official standing, and consequently no professional responsibility; are not in the same class as other professional men, such as druggists, doctors, lawyers, engineers, or ministers.

Now is the time, right now, to start something, while we are still in the public eye, when blame or credit is given us for at least having been involved in the war's activities. To-day the public and the press are still impressed with the "supreme" importance and value of chemistry, if only as a war science. We have a strong numerical and very influential backing of the other unrecognized profession, that of the cooks, who have been so dependent on us, through our scientific control of their raw materials. No one will forget the slogan, "Food will win the war." We backed the cooks, some 20,000,000 kitchen soldiers, and taught them more about foodstuffs and feeding in 18 months than they had been taught during our whole previous existence from 1492. Chemical terms such as calories, proteins, fats, carbohydrates, and vitamines are to-day common household words, and even in the kindergarten they know what the chemical verb "to hooverize" means.

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[1] THIS JOURNAL, **6** (1914), 689

In September 1914 I spoke to the Chicago Association of Commerce[1] and in December before this Institute[2] using the same title for my paper as of to-day, without the word "Reconstruction." Conditions have not changed, except in so far as temporary war measures have, for the time being, modified them, and unless we can make many of these temporary measures permanent, we shall drop back into the same old rut. The statement of the past will apply to our future, that "In many cases, not all, Federal requirements so restrict us as to actually prohibit us from manufacturing and going into competition with, and replacing imported articles. Patent, trademark, and copyright acts, with internal revenue acts, stand in the way, firmly braced by the Sherman Act. You can convince yourselves of this by a study of those (chemical) industries in the United States where this interference, this prevention is not felt." The "Trading with the Enemies" Act gives some relief, annulling temporarily our patent and trademark acts, but this is limited, requiring a government license, with safeguards to protect the former owners, as to profits and royalties. Restrictions under the Sherman Act, the Interstate Commerce Act, the Foods and Drugs Act, and others, are partly annulled, for the time of the war, and perhaps for a limited time thereafter, but some of these privileges are already withdrawn, and many of those active in their enforcement have received very complimentary letters of thanks for past services. Powers delegated to the War Finance Corporation, Emergency Fleet Corporation, War Industries Board, War Labor Board, Food, Fuel and Railroad Administrations, Chemical Warfare Service, and other similar bodies should not be given up, without substituting something, at least during the reconstruction period.

The Webb-Pomerene act is a permanent measure and no doubt will be of commercial importance, although it sets up a dual standard for doing business. It nullifies the Anti-Trust acts, allowing combinations or trusts in the United States, but only as far as export trade is involved. If it is a good business policy to allow trusts or combinations to obtain a foreign market, why will it not be of equal benefit to allow regulated and controlled combination at home to enlarge and hold the home market? Would this not enable us to meet foreign competition at home better, especially if we protect manufactured products and raw materials? In effect this act allows us to combine to dump our goods in certain foreign markets, but in no way prevents foreign goods from being dumped on us. This dual standard for doing business may bring about the conditions that we can re-import, duty-free, exported manufactured products, at a lower price than we can get them at source of manufacture. This act may become a boomerang if not a Frankenstein.

At the Paris Economic Conference, as early as September 1916, a plan was considered by the Allies to restrict the markets of the Central Powers, and it was proposed to deprive German industries of raw materials, by conserving for themselves "their natural resources and establishing social arrangements to facilitate interchange of these resources." Commercial history shows that national trade wars are as destructive as military wars, but that measures of defense are necessary to prevent a nation's manufactured products from discrimination. We have magnified or exaggerated the importance to us of foreign markets for our raw materials, as compared with our manufactured products. If we are a market for the whole world, why not make the world our market for our manufactured products? We can do so by restricting exports of and interchanging of raw and natural resources. We must consider the opposite of a Webb-Pomerene Act, an Anti-Dumping Act, adequate to protect American business from unfair foreign methods, and this is more of a necessity for the chemical industry than any other.

It was a chemical war, and must be a chemical reconstruction. As to some of the exclusively chemical problems before us, only a superficial and very narrow review can be attempted. Individual cases cannot now be considered, such as changing a synthetic phenol factory into one making rose oil or vanillin extract, and the rebuilding of a flexible glass works into one making non-losable golf balls, is of minor importance.

Our most important chemical reconstruction should come in the teaching of chemistry, not alone in our universities and colleges, but in our preparatory schools. Dr. Henry S. Pritchett, President of the Carnegie Foundation for the Advancement of Teaching, in the preface to Prof. Chas. R. Mann's bulletin on "A Study of Engineering Education, 1918," very forcibly says:

> In the half century that has passed, this course of study (engineering) has been overlaid with a number of special studies intended to enable the student to deal with the constantly growing application of science to industries. While the original plan remains as the basis of the teaching in the four-year engineering curriculum, the course given in most schools has been greatly modified in the effort to teach special subjects. As a result, the load upon the student has become continually heavier and bears unequally in different places and in different parts of the course. In addition there is a wide-spread feeling that under this pressure the body of the students will fail to gain, on the one hand, a satisfactory grounding in the fundamental sciences; and on the other hand, do not fulfill the expectations of engineers and manufacturers in dealing with the practical problems with which they are confronted on leaving the engineering schools.

Have not the last two years shown that this applies as strongly to chemistry as to engineering? We all know that before the war there was a strong fence dividing the theoretical, research, and pure chemical scientist from the practical, commercial, and industrial chemist. A few outsiders, some connected with technical schools, some in large laboratories, and some individuals, straddled the fence, seldom doing anything to bring the two factions together, often in fact finding it to their advantage to keep them apart. Commercialization of chemical science was abhorrent to many teachers of chemistry. The pre-war German chemical preëminence was due not to any super-capability or super-mentality of her teachers of chemistry or other sciences, but to their utilizing and developing *industrially* every advance in scientific knowledge. No one can point out any new fundamental discoveries made by German scientists within the past forty years. Laws of chemistry and physics were discovered by Dutch, Norwegian, English, French, Italian Japanese, Canadian, and American men of science. Many scientific discoveries have been claimed by the Germans, who simply appropriated them, and developed and applied them in their industries.

But the change in our teaching cannot be confined to our educational institutions, it must also embrace our employers and employees. We must develop a scheme for adequate training of workers so that their versatility, efficiency and productivity will be increased—a mutual advantage to capital and labor. We must have an association between labor and capital, not alone practical and physical, but also mental and educational.

We had different classes among our chemists some two years ago, and the contempt shown each other by the members of these factions was mutual. There is to-day no chemical laboratory, collegiate or university, corporation or private, whose chemical staff was not temporarily badly disrupted by the war. These chemists, men and women, are returning to their pre-war industries and activities, and they will insist on a radical reconstruction in the chemical curricula of our institutions.

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[1] Chicago Assoc. Commerce, *Bulletin*, October 1914.

[2] This Journal, 7 (1915), 151

We are sure that our new mutual comrade in chemistry, Prof. X. Y. Z., having served our Government, perhaps having perfected a new waterproof coating for airship wings, assisted by a former stock-yards chemist, or having supervised the making of deep-sea bombs, with the help of a fermentation expert, or reconstructed a gas mask, coöperating with a fuel specialist, will not be satisfied to accept for a doctor's degree a thesis describing a new compound containing 23 13/19 carbon radicals, arranged in a parabolic curve, and some 57 varieties of salts made therefrom, all ready to be nicely hidden away in the cellar of the chemical museum of his Alma Mater; nor will the practical chemical cuss run and dodge, or take the other side of the street, when he sees Prof. X. Y. Z. in the far distance. This war has conclusively shown us that "real genuine research work and chemical manufacturing experience go together, are absolutely dependent on each other, and are the foundation of the development of chemical industries."

Reconstruction in the teaching of medicine must also come, and it must follow chemical lines. Recent medicine is directly chemical. Preventive medicine depends on products originated and produced in the chemical laboratory, whether a direct active medicinal preparation, or a serum or anti-toxin. Internal medicine is based on chemical and microscopic analysis, which may consist in a blood count, analysis of stomach contents, or the making of a direct coal-tar color in testing the urine by the indol reaction. The first treatment of the wounded on the battle-field is chemical, involving the use of iodine, and in the base hospital the Carrel treatment with the Dakin solution depends on the action of chlorine. The excellent health conditions in our Army and Navy, at our camps and cantonments were due to chemical means, even if camouflaged under the name of sanitary methods.

Little authentic information is at hand as yet in regard to the damage done through the illegal, brutish, foul and inhuman use of poisonous and noxious gases. Prospective medicine will have to consider the effects caused by these chemical death-dealing and health-destroying gases, but it is not improbable that within a reasonable time these and other chemical gases may be used legitimately as health-restoring agents, especially against infectious diseases of the respiratory organs, and diseases transmitted to the system through nose or mouth. It may be wrong to draw the conclusion, but the suggestion is not out of place, that the relatively small number of cases and fatalities, due to influenza, among the allied troops on the Western front, was partly due to the peculiar antiseptic character of the atmosphere there, both on account of the poisonous antiseptic gases used in warfare and also the gases generated by the ammunition exploded. This view is supported by the meager circumstantial evidence that at the second battle of the Marne, the turning point of the war, the German advance was retarded for 10 to 15 days, due to the epidemic of influenza among her troops. *The allied nations did not make use of intensive gas warfare at that time.* A little, not very authentic, data is also at hand, indicating that workers in plants making war gases, mainly chlorine, were more immune against infectious diseases than others in the same communities, and the same thing seems to be indicated for workers in other chemical industries where active gases pollute the atmosphere.

According to Dr. F. Tweddell,[1] "certain occupations are comparatively free from the curse of phthisis and others are immune to it. On page 98 of Fishberg's 'Pulmonary Tuberculosis' we find, 'coal dust prevents the development of phthisis, and that miners are less subject to phthisis than all other occupied males.'" Dr. Tweddell suspected sulfurous acid gas as the cause of this immunity. In this connection many of us remember our grandmother's treatment for whooping cough and throat troubles, sending the children to coal-gas works to play in that polluted, antiseptic atmosphere. Many cases could be cited to show how dependent present-day medicine is on chemistry, its products and processes, and that a reconstruction in medicine and its teachings must be along chemical lines.

A chemical influence in the reconstruction of teaching some underlying principles of law can also be anticipated, if only so far as to have expert testimony confine itself to actual facts, rather than to precedents based on the scientific fancies and follies of the legal profession.

An inoculation of some chemistry into theology is also not out of place, especially in calling attention to the fact that the right way of living, the use of certain foods, and the abstaining from others, and certain religious sanitary laws are based on chemical facts.

Agriculture, production, distribution and conservation of the products of the soil, is strictly a chemical consideration, and we should be active in solving the many agricultural problems that our reconstruction program will have to consider. We never again should become as extravagant in the use of our food products as we were before the war. The economical principles we were taught and practiced should remain a part of our national custom. Four pounds of sugar per month will satisfy the most fastidious sweet tooth and a return to about 90 pounds per capita per year will again be wilful waste. We got along very well when using a greater amount of cereals, rice, cornmeal, home-grown vegetables, and lesser amounts of meats. The Government has recognized the necessity of stabilizing our agricultural industries through guarantee of a minimum price for crops grown during 1919. We need only consider one real chemical industry to show the chemist's interest and place as to agriculture.

Before the war we depended on foreign nations for the greatest part of our nitrogen and potash fertilizers. We had phosphoric acid in the form of natural phosphate rock. This natural raw material we exported in very large amount, shipping it as ballast from southern ports. We took part of it back, after the phosphoric acid had been made available, paying a high price for this simple chemical transmutation. Although we did use some of this phosphate rock ourselves, we never exported any phosphate fertilizers. As to nitrogen fertilizers, we actually paid tribute to foreign nations, and furnished the dividends for the British niter trust. Our main nitrogen fertilizers came from Chile, as guano, often after having crossed the ocean twice, with stop-overs at Hamburg or Bremen, or English or Dutch ports.

Potash salts we had none except those imported. We used many in our industries and laboratories, which we have since replaced with sodium salts. This unnecessary use of potassium compounds was fostered through the propaganda of the German alkali trust. To-day we are home producers of potash salts. Are we going to construct a program that will enable these home industries to continue?

We can anticipate a surplus manufacture of nitrogen and potash fertilizers and other similar products, and must develop a system that will take care of these industries. We cannot kill off the development of our potash deposits and potash kelp industry, nor should our potash recovery in steel mills and cement plants be given up. While our steel and cement industries will live and prosper without a recovery of potash salts from their flue gases, we cannot allow them to waste these products. Nothing definite can be stated to-day as to our natural potash deposits, as they are still in the initial stage of development. The kelp potash industry is undergoing a radical change, and the potash recovered is becoming a by-product, the main products being those obtained from "wood" distillation and iodine recovery. Our nitrogen fixation plants will have to compete with the by-product coke industry and the gas-house nitrogen plants.

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[1] *Medical Record*, December 21, 1918.

We must bear in mind that these new nitrogen and potash plants give us really *new* sources of supplies, commercially non-existent before the war. Our production, therefore, is in excess over the world's pre-war production and we have substituted our own products for those we formerly imported. We must look for a greater production right along and must enlarge our home consumption to take care of our own products of manufacture. We cannot expect any export business, as our lessened imports will increase available stocks in foreign countries. The nitrogen products from our government nitrogen fixation plants are to be taken care of by the Nitrate Division, through the Department of Agriculture, who expect to sell during 1919 about 300,000 tons of nitrate of soda to farmers, at cost price on board of cars at loading points. With a proper reconstruction program, our fertilizer industries can also be free from importations. The proper protection of our nitrogen industries has direct bearing on our dye industry, as its source of raw material is the same, coal-tar and coke industries. In 1917 we manufactured an excess of dyes over our American needs, and exported United States dyes of the class formerly imported to the value of $11,709,287, exceeding in value our pre-war importations, although we did not equal our former imports in tonnage or in variety of colors. The 1918 value for dyes exported is given at $16,921,288. The total amount of dyes made in the United States for 1917 is valued at $57,639,901.[1]

The industrial chemist must not forget that to-day we are perhaps the only credit nation on the surface of the earth. We cannot expect to export products which we formerly imported, without seriously affecting trade balances, especially if at the same time we curtail our imports through home manufacture. To maintain a necessary equilibrium in trade we must buy as well as sell, we must create liabilities to make good our assets. In all cases we shall have to meet strong competition from our former war allies, our present friendly trade enemies, who are to-day ignoring as far as they can our agricultural products, going to the Southern Hemisphere, Australia, the Far East, and Africa for wheat, sugar, meats, leather, wool, cotton, and other products of the soil. To uphold our agricultural industries and those depending thereon, we must have protection, free trade, or a tariff for revenue, the proper financial assistance, a correct government control, regulation or ownership, or at least a partial government partnership in industry, with or without subsidies. We must look to our own home market for our greatest demand and must protect this so as to hold it absolutely against all outsiders, and we must have a fair return on invested labor and capital. Under no condition can we allow our country to become a dumping ground for any foreign commodity, notwithstanding that the Webb-Pomerene act allows us to do to others what we don't want them to do to us.

These requirements hold good for many chemical commodities: products from our glass, china, porcelain, clay, and ceramic industries; it holds good for our coal-tar industries, dyes, colors medicinal preparations, flavors, perfumes, solvents; it does not differ for our food, fuel, petroleum, rubber, wood, textile, or paper industries; it applies to our metal and alloy industries; in fact, to every industry where chemistry is or can be involved. It applies to every industry whose products we formerly imported, and for all products for which we have found a suitable United States substitute.

It will not be many months before the devastated territory of France and Belgium will be rehabilitated and again productive. America is helping not alone with food and money, but is actually rebuilding many industrial concerns, on American foundations and according to American methods. What the American Army and Navy did in France is bearing fruit among the people of France and Belgium and they have learned a lesson through observation. They see before them the marvelous picture of a community of about $2^1/_2$ million people created within 18 months, everything, people and supplies brought from 3000 miles away. Future history will designate this work of our Army and Navy (and much of it was chemical) as the eighth wonder of the world, greater than the combined seven wonders of past history. These American methods of doing things are incorporated in the rehabilitation schemes of those countries and their application will greatly shorten the time of recovery, bring them so much more quickly into a productive stage, and so much sooner into the world's markets and into competition with all their war allies. American steam shovels, portable saw mills, traction engines, and many chemical reclamation tools are used in the French and Belgium reconstruction programs, which call for extension of canals, new water- and roadways, reforestation and every other means to make their lands more productive and fitter places to live in. This has been a chemical war and will be a chemical restoration. We chemists cannot again be given places on the last row of the top gallery, in this great world's show. We have been actors, in the spotlight, holding the center of the stage. We are to-day strong and our existence is recognized, and we stand where we stood five years ago. "The chemists of the United States have the brains and the ability and the gumption to make it—not 'Made in America' but 'Made in the U. S.' All the chemists in the United States need and all they again ask for is the opportunity, fair play and an open field, not fenced in with adverse legislation."

We have now the opportunity and can do our part in seeing that chemical industry allows every one of our returning fighting boys to return to his pre-war activities. We have the chance to do our part in the reconstruction of our educational systems. We must be an active force in solving problems as to health and social economic conditions. We must be a strong factor in the development of our agricultural interests and the industries depending thereon. We must enforce our views for the protection of all new and newly developed chemical industries. We must exert ourselves in regard to the conservation and utilization of our raw materials and our natural resources, and in the production and distribution of our manufactured products. We must become a vital part in a real chemical reconstruction program.

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[1] U. S. Tariff Commission Census of Dyes and Coal-Tar Chemicals, *Information Series* 6.

NITROCELLULOSE FROM WOOD PULP[1]

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INTRODUCTION

Considerable interest was aroused in 1915 by press notices that the Germans were successfully using wood cellulose in place of cotton cellulose in the manufacture of smokeless powder. Due to shortage of cotton in Germany caused by the blockade it was absolutely necessary for them to turn to this source for nitrating material. It can be readily appreciated that with the enormous supplies of short-fibered cotton available in this country for nitrating purposes there appeared to be no possibility whatsoever that this country would be placed in the position of having insufficient cotton for smokeless powder manufacture, or have to figure on the use of wood cellulose to supplement its supply of cotton. The object of this paper is to give some idea as to how the Government and the powder manufacturers together were prepared to meet this emergency, which actually arose a few months before the signing of the armistice.

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[1] Read before the New York Section of the American Chemical Society, Chemists' Club, New York, N. Y., November 7, 1919.

HISTORICAL

The attempt to produce nitrocellulose from wood dates back to the year 1865. During that year an article appeared by a Prussian artillery officer, Edward Schultze, in which was noted the preparation from wood of an explosive and propellant. In the years 1870 and 1871 Volkmann improved this so-called "white powder" by gelatinizing the nitrocellulose with an ether-alcohol solution. Although this Schultze powder was not suitable for military purposes, it attained a great degree of popularity as a sporting powder.

The United States, as is generally known, was the last of the world powers to adopt smokeless powder for military use in place of black powder. As the nitrocellulose used in foreign smokeless powders was at that time made from cotton, and as there was an aversion to the use of wood cellulose, it was quite natural that the smokeless powder industry in this country should have been initiated with the use of cotton cellulose as the raw material for nitrocellulose.

Carl Schwalbe[1] states:

> Up to the present time nitrocellulose used in different industries has been prepared almost entirely from cotton, although wood cellulose in sufficient amount and in a suitable physical condition has been available at a lower price; furthermore, the wood cellulose is produced in Germany while cotton must be imported. Nevertheless the more expensive cotton is given preference because pure nitrocellulose is more easily obtained from pure cotton cellulose and because the existing impurities in the wood cellulose in all probability exert an influence on the stability and on the process of stabilization.

By far the most important reason why wood cellulose was not used in place of cotton for smokeless powder manufacture was the question of chemical stability of the powder during storage. This has always been a very vital problem, affecting as it does the safety of officers and men of our Army and Navy, besides the safety of property. While there are various stability tests at elevated temperatures which give an indication, in a relatively short time, of the stability of a powder and afford a very useful criterion of the quality, its stability is largely gauged by what occurs in actual storage. Inasmuch as too little has been known regarding the chemical stability of smokeless powder under various conditions, and since diphenylamine was not adopted by this country as the stabilizing agent until 1909, it can be appreciated that government officials have been very reluctant even to consider a change to some source of cellulose other than cotton, without the most thorough investigation, covering observations of powders during many years of storage under varying conditions.

As far back as 1909, however, a survey of the subject indicated the possibility of economy due to the lower cost of wood pulp as compared with cotton. At this date several articles had been published in the literature, largely by the Germans, which were not particularly encouraging as regards the use of wood cellulose, indicating lower yields of nitrocellulose, greater consumption of acid, and questionable stability. In 1915, when it was announced that the Germans were successfully using wood cellulose for nitrocellulose in place of cotton, it was planned in our laboratories to nitrate on an experimental scale a few hundred pounds of wood cellulose, purify the product, and manufacture the same into powder for ballistic and chemical tests, although it was not thought then that there would ever come a time when the amount of cotton available in this country would be less than the amount required for war purposes.

Great difficulty was met in obtaining wood pulp suitable for nitrating purposes. Although a great many samples were obtained from various manufacturers, all indicated insufficient purification treatment, severe overbleaching, and entirely unsuitable physical condition. However, with a great deal of difficulty, due largely to unsuitable physical condition of the wood pulp, about 50 lbs. each of sulfite and soda-wood pulp were nitrated in laboratory equipment, the nitrocellulose purified according to government specifications, and made into 0.30-cal. and 1-pounder powder. The results of stability and ballistic tests were very encouraging. The unsuitable quality of wood cellulose from the standpoint of chemical purity and composition as compared with cotton and the unsuitable physical condition impressed us with the need of large-scale experiments in order to obtain data regarding manufacturing difficulties in the nitration of the wood pulp, purification of the nitrocellulose, and its manufacture into powder.

During 1917 the development of the problem of using wood cellulose on a large scale was greatly facilitated by the fact that specially purified soda and sulfite wood pulp were obtained in suitable quantity.

Acknowledgment is here made of the assistance given by the West Virginia Pulp and Paper Company of New York in preparing at our request special lots of purified soda and sulfite wood pulp; and also of the assistance given by the Forest Products Laboratory, of Madison, Wis., in furnishing us information in regard to available supplies of wood and the purification treatment received by the various woods in the preparation of commercial wood pulps.

BRIEF OUTLINE OF SMOKELESS POWDER MANUFACTURE

The first step in the process of manufacture of smokeless powder is the purification of the cotton by digestion with 2 per cent caustic soda solution for 4 or 5 hrs. at 75 to 80 lbs. steam pressure. The digester charge is then blown over into a wash tank to remove the waste liquor. The cotton is bleached with a very weak solution of bleaching powder and washed several times with water. It is then run through squeeze rolls to remove a part of the moisture, picked to open up the fiber, and finally run through the cotton driers until the moisture content is reduced below one per cent. It is next nitrated for about 30 min. in a mechanical agitator, dumped into a centrifugal wringer, and the excess of acid removed by wringing for about 3.5 to 4 min. The nitrocellulose, containing about a pound of acid for every pound of nitrocellulose, is then dumped into a drowning basin containing a large quantity of water and thence pumped to the boiling tubs. It receives a preliminary boiling treatment in acidulated water for about 40 to 45 hrs. which serves to hydrolyze and break down the unstable esters, especially the sulfuric esters; is then pulped by means of beaters or Jordan engines; and after pulping receives a poacher boiling treatment, divided into several treatments of a total duration of 12 hrs. The purified nitrocellulose is then wrung in centrifugal wringers until the moisture is reduced to about 30 to 33 per cent. This operation completes the preparation of the nitrocellulose for smokeless powder manufacture.

The next process in the manufacture of smokeless powder is the removal of the water in the nitrocellulose by means of alcohol. A charge of wet nitrocellulose is formed into a block in a hydraulic press by means of low pressure of about 250 lbs. per sq. in. About 50 lbs. of alcohol are pumped through a perforated screen in the head of the press, and as it passes down through the nitrocellulose displaces the water. To remove the excess alcohol the block of nitrocellulose is pressed under a pressure of about 3,000 lbs. per sq. in. until it contains the desired amount of alcohol, as predetermined by weighing a block of dehydrated nitrocellulose and marking the size on the telltale.

The blocks are then sent to a block breaker, consisting of a revolving screen of very heavy wire containing balls which break up the block into small pieces. The charge of nitrocellulose is then placed in the mixer and treated with sufficient ether so that to every 100 lbs. of nitrocellulose there are about $33\frac{1}{3}$ lbs. of alcohol and $66\frac{2}{3}$ lbs. of ether. Diphenylamine, which is used as a stabilizing agent, is previously dissolved in the ether. The mixer is provided with brine refrigeration to prevent loss of solvent. The mixing of the nitrocellulose requires about 30 min. at the end of which time a mealy looking colloid is obtained. This is formed into a block about 12 in. in diameter and 16 in. high, at a pressure of about 3,000 lbs. Three blocks of this size constitute a charge for the finishing press, where the colloid is pressed through dies and granulated on cutting machines into grains of various sizes, according to the caliber of the gun. The grains then receive a treatment of several days in order to remove and recover the excess of solvent. The powder is next treated in a tank of hot water at about 55° C. for several days until the solvent content is reduced to the amount desired, when the excess of water is removed by air drying. The powder is then taken to large blending towers and in lots of 100,000 lbs. each given a very thorough blending. Ballistic and chemical tests are finally made on representative samples of the lot of powder.

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[1] *Z. angew. Chem.*, 1 (1914), 662.

NITRATION OF WOOD PULP ON LARGE SCALE—PRELIMINARY EXPERIMENT

The processes of manufacture in which it was expected that the use of wood-pulp cellulose would give difficulty were in the nitration and purification of the nitrocellulose and in its dehydration and colloiding. Early in 1918 it was decided to nitrate about 1,200 lbs. of sulfite wood pulp in the regular nitrating equipment in order to obtain some information about the difficulties which would be met in nitrating wood pulp in regular factory installation. This wood pulp, in crepe paper form, gave considerable difficulty in nitration. There was a tendency of the nitrated material to gelatinize during nitration, and owing to this and to the shortness of the fiber the wringing of the acid from the nitrocellulose in the centrifugal wringer gave great difficulty. The yield of nitrocellulose was very low, only 1.2 lbs. of nitrocellulose per pound of wood cellulose, as compared with 1.5 lbs. when nitrating cotton. The consumption of acid was high, due to difficulty in wringing the acid from the nitrocellulose. Considerable difficulty was also found in the dehydration of the nitrocellulose. Due to the very finely divided condition of the material it required almost 50 per cent longer to pump the alcohol through and to remove the excess alcohol. It was found, as was expected, that the viscosity of the wood pulp nitrocellulose was much lower than that prepared from cotton, the amount of solvent required for colloiding being about 8 per cent less than when using nitrocellulose prepared from cotton.

The above experiment impressed us with the serious mechanical difficulties involved in the use of wood pulp for nitrocellulose and the necessity for a thorough chemical comparison of wood cellulose with cotton cellulose.

COMPARISON OF COTTON CELLULOSE AND WOOD CELLULOSE

As previously stated, wood pulp prepared for paper making is not sufficiently purified or in a suitable physical condition for nitrating.

With reference to the specifications for purified cotton for nitrating purposes the War Department requires it

> To be bleached cellulose prepared for nitrating which will be obtained by purifying unspun cotton waste or suitable short-fibered commercial cotton and thoroughly washing to remove the purifying material or salts.
>
> To contain not more than 0.4 per cent of ether extractive matter, not more than 0.8 per cent of ash, and not more than traces of lime, chlorides and sulfates, nor more than 7 per cent KOH-soluble material.
>
> To be of absorbent and uniform character, clean and free from such lumps as will prevent uniform nitration; to contain as little as possible of felted fiber and dust, technically known as "fly;" to be free of motes, flues, sweepings, hull fiber, or other foreign matter.
>
> Moisture must not exceed 7.0 per cent.

It may be of interest to note that these specifications were very misleading to pulp manufacturers, many of whom furnished samples of wood pulp which complied with the specifications as regards ether extractive matter and ash, but did not appreciate that the specifications were meaningless when applied to anything but cotton. The specifications in regard to KOH-soluble matter were not incorporated in the government specifications until the latter part of 1918, although this specification had been used for many years by us. While these specifications were sufficient to cover the purity of cotton cellulose they were unsuitable for wood cellulose.

Wood belongs to the widely distributed class of lignocelluloses of which jute probably represents the purest form. In addition to lignocellulose as the main constituent, hemicelluloses, *i. e.*, the pentosans, are always present in wood; while resins, gum, tannin, carbohydrates, dyes, ethereal oils, etc., occur as secondary constituents. Wood pulp requires a much more drastic cooking treatment than cotton cellulose to remove these impurities. Moreover, the purified wood cellulose is considerably different in chemical composition from cotton cellulose. This difference is strikingly brought out by the method of Jentgen, extensively used by Cross and Bevan, of dividing cellulose into three types: α, which is insoluble in cold 17 to 18 per cent caustic soda solution when treated for 30 min., β, that portion which is dissolved by the caustic solution but reprecipitated on the addition of acetic acid, and γ, that portion which is dissolved by caustic but not reprecipitated on the addition of acid. Applying this method of analysis to purified cotton such as is used in smokeless powder manufacture, we find that it consists of approximately 94.5 per cent α-cellulose, 3.0 per cent β-cellulose, and about 2.5 per cent γ-cellulose. If the cellulose is very strongly bleached, severely digested, or both, the tendency is to increase the β-cellulose; for example, a long cooked and well bleached cotton gives 81.0 per cent α-cellulose, 16.0 per cent β-cellulose, and 3.0 per cent γ-cellulose. We know that in cotton cellulose the γ-cellulose is lost during nitration but that the α- and β-celluloses are converted into nitrocellulose. As shown by Piest and others overbleaching gives nitrocellulose more difficult to stabilize, so that specifications for cotton for smokeless powder manufacture prescribe that overbleaching is to be avoided.

The chemical composition of the cellulose in soda and sulfite wood pulps differs from cotton cellulose. For example,

	α-Cellulose Per cent	β-Cellulose Per cent	γ-Cellulose Per cent
Unbleached sulfite pulp from spruce...	85.0	7.0	8.0
Mildly bleached sulfite pulp from spruce..........................	87.0	3.0	10.0

It will be noted that sulfite pulp, bleached or unbleached, usually contains about 8 to 10 per cent of γ-cellulose which is of no value for nitrating purposes. Small-scale digestions in the laboratory indicated that most of the γ-cellulose and a portion of the β-cellulose in sulfite pulp, either bleached or unbleached, could be removed by digesting with caustic soda solution under pressure, and that the resulting product would approach more closely to the composition of cotton cellulose. This is shown by the following comparison:

	α-Cellulose Per cent	β-Cellulose Per cent	γ-Cellulose Per cent
Purified cotton......................	94.5	3.0	2.5
Mildly bleached sulfite from spruce, digested 5 hrs., 80 lbs. pressure, 2 per cent caustic soda solution........	95.0	2.0	3.0
Unbleached sulfite from spruce, redigested as above..................	94.5	2.0	3.5

Soda pulp, on the other hand, naturally contains less γ-cellulose because of the alkaline digestion treatment, but the amount of β-cellulose is very much higher than in the case of sulfite wood pulp, even in the unbleached material.

	α-Cellulose Per cent	β-Cellulose Per cent	γ-Cellulose Per cent
Bleached soda pulp from Jack pine....	67.0	26.0	7.0
Same, redigested 5 hrs., 80 lbs. pressure, 2 per cent caustic soda solution.....	85.0	13.0	2.0
Unbleached soda pulp from Jack pine..	86.0	10.0	4.0
Same, redigested with caustic soda solution, under pressure as above...	84.0	14.0	2.0

The unbleached soda pulp contains considerable colored products which are not removed by digestion with caustic soda solution and give a very dark nitrocellulose. Furthermore, these colored products give a very dark smokeless powder. If the soda pulp is bleached and redigested with caustic soda, the color of the pulp is very materially improved, owing to the removal of the colored products which are made more soluble in alkali by chlorination. Briefly, while sulfite and soda pulps as prepared for paper manufacture are not purified sufficiently for nitrating purposes, further digestion under pressure with caustic soda solution, preceded in the case of soda pulp by a mild bleaching to improve the color, will give a cellulose more nearly approximating the chemical composition of cotton cellulose, except that the soda pulp will have a higher β-cellulose content than cotton.

Another important difference between wood and cotton cellulose is the length of the individual fibers. Second cut linters will have a maximum length of about 25 mm., a minimum of 0.80 mm. and an average of about 4.6 mm. Hull shavings will average about 2.4 mm. with a maximum of 8.00 mm., depending on how much linters have been removed from the seed, and a minimum of 0.5 mm. Wood fiber from coniferous woods will usually have an average length of about 2.5 to 4.0 mm. Reference has already been made to the difficulty experienced in the nitration of a small lot of sulfite wood pulp in regular factory equipment. It should be appreciated that the factory apparatus for nitration, purification of nitrocellulose, and its manufacture into powder are the result of a gradual development covering a period of more than 20 years. A number of years ago experiments demonstrated considerable mechanical difficulties in using hull shavings alone, due to the tendency of the short fiber to dry harsh, and the difficulty of wringing out the excess acid after nitration. It was found at that time that the addition of 30 per cent or more of the linters to the hull shavings greatly facilitated the drying of the short fiber in suitable physical condition for nitration, and also the wringing out of the excess acid. For a number of years previous to the war it was the standard factory practice to use a mixture of linters and hull shavings for nitrocellulose.

We have already referred to the unsuitable physical condition of wood pulp for nitrating purposes. Cellulose in harsh paper form cannot be nitrated as the acid does not readily penetrate the material. It is necessary that the cellulose be absorbent and preferably in fibrous form or very thin sheets, in order that the proper nitration of the cellulose can be obtained. While it was appreciated that wood pulp prepared in tissue or crepe paper form could be dried in fairly soft condition for nitration, this would have involved the manufacture and installation of special machinery by the paper manufacturers, and, furthermore, the nitrating equipment in our factories was not suitable to handle wood pulp in this form.

Numerous experiments were made in an endeavor to produce a softer wood cellulose, and one which could be dried in bulk like cotton, by digesting the wood under milder conditions than used for paper making purposes. While this produced a slightly softer fiber, the difference was too slight to be an important factor. It was accordingly decided to experiment on the use of wood pulp by blending it with cotton fiber before use.

Accordingly a number of factory experiments were made with mixtures of cotton fiber and sulfite or soda wood pulps. It was found that at least 50 per cent of wood pulp could be used in the mixture without seriously affecting any operation in the manufacture of smokeless powder. This was very gratifying in view of the magnitude of smokeless powder manufacture.

The idea as finally developed was to obtain carefully purified sulfite pulp from paper manufacturers, prepared largely from spruce, or mildly bleached soda pulp prepared from Jack pine wood instead of a deciduous wood, as the latter appeared to be less suitable for nitrating purposes. The preparation of this material by the wood pulp manufacturers would have required no important change in their process of manufacture. It was proposed to consider this as raw material equivalent to linters or hull shavings and to digest it simultaneously with linters and hull shavings under pressure for about 5 hrs. at 80 lbs. pressure, with approximately 2 per cent caustic soda solution. In the case of unbleached sulfite wood pulp we expected a loss on digestion of about 20 to 25 per cent and in the case of mildly bleached soda pulp a loss of only 10 to 15 per cent. The purified mixture of cotton and wood cellulose was to be dried, nitrated, and purified in regular factory equipment.

Following preliminary experiments which showed that the mixing of about 50 per cent linters with the wood pulp eliminated almost entirely the difficulties in connection with the manufacture of nitrocellulose and powder from the wood pulp, arrangements were made with the Government to manufacture 100,000 lbs. of 3 in. field gun powder from a mixture of 50 per cent sulfite wood pulp and 50 per cent linters. This mixture of sulfite wood pulp and linters was digested in regular factory equipment. The wood pulp was received in rolls about 24 in. in width and was simply cut longitudinally and charged into the kier together with the linters. The hull shavings were omitted in the experiment in order to obtain more accurate figures with reference to the yield of purified wood cellulose and the yield of nitrocellulose from the wood cellulose portion of the mixture. The mixture of linters and wood cellulose gave practically no difficulty in nitration; the acid recovery was normal and the yield of nitrocellulose was about 1.50 lbs. per pound of cellulose, as compared with about 1.52 lbs. for cotton. This indicated a yield of about 1.48 lbs. of nitrocellulose per pound of sulfite wood cellulose.

The nitrated material received the regular government purification treatment. The pulping of the nitrocellulose was found to require slightly shorter time due to the shorter wood fiber. The stability of the nitrocellulose was found to be very satisfactory indeed.

This material was made up into 3 in. field gun powder. In the manufacture of the nitrocellulose into powder it was found that the nitrocellulose dehydrated about 10 per cent more slowly, a difficulty which could be taken care of in the manufacture by the installation of additional dehydrating presses to make up for the loss in output. The nitrocellulose required slightly less solvent, due to the fact that the viscosity of the nitrocellulose from the wood pulp was lower than the viscosity of the nitrocotton.

The general conclusion reached from the manufacture of this 100,000 lbs. of nitrocellulose and of powder from the mixture of linters and wood pulp was that there were no serious difficulties which could not be overcome. The ballistic tests of the finished powder showed the product to be the equal of powder made from nitrocotton.

SHORTAGE OF COTTON

Up till about July 1918 it was not anticipated that any wood pulp would be needed, in spite of the enormous production of smokeless powder proposed for the balance of 1918 and for 1919, with the Old Hickory Plant at Nashville and the Nitro Plant beginning to come into operation. On the first of August, however, the Department of Agriculture forecast a most serious drop in cotton yield owing to the drought. A conference was immediately called at Washington by the War Industries Board and it was pointed out that owing to the cotton shortage, instead of using a mixture of 70 per cent linters and 30 per cent hull shavings, it would be necessary to use a mixture of about 63 per cent linters, 23.5 per cent hull shavings and 13.5 per cent wood pulp, with the prospect that the amount of wood pulp would have to be very materially increased. The program of the War Department figured on the use of 150,000 tons of sulfite wood pulp for the ensuing year, or 500 tons per day, approximately 10 per cent of the output of sulfite wood pulp.

On the basis of the large-scale experiment above described it was recommended that preliminary to putting the entire manufacture of smokeless powder in this country on the cotton-wood pulp basis, we should immediately manufacture 1,000,000 lbs. of powder each, from a mixture of 50 per cent linters, 25 per cent hull shavings and 25 per cent sulfite wood pulp, and a mixture of 50 per cent linters, 25 per cent hull shavings and 25 per cent soda wood pulp.

At the time of the signing of the armistice, all preparations were made for the nitration of the material. The order for the manufacture of the powder was immediately cancelled, so that we were prevented from obtaining very valuable data as regards yields and manufacturing difficulties, and a satisfactory comparison of sulfite and soda wood pulp.

We believe that a very satisfactory powder could be made from either sulfite or soda wood pulp and that the advantages or disadvantages of these two materials as regards difficulty in manufacture, yields, etc., could be obtained only from large-scale manufacture such as we recommended. We also wished to place ourselves in a position so that we could use either soda or sulfite wood pulp in case of shortage of material.

With reference to the kind of wood, coniferous woods appeared to be more suitable because of longer fiber, so that in the case of sulfite pulp we were specifying largely spruce and, in the case of soda pulp, Jack pine. On the advice of government experts and private manufacturers we confined our attention almost wholly to the use of coniferous woods. Information from Germany indicated that they were probably using sulfite wood pulp and examination of several samples showed two to be entirely spruce and the third about 75 per cent spruce and 25 per cent pine. Other information stated that soda and sulfate wood pulps were being used by Germany and it is quite possible that all three kinds were finally used.

USE OF WOOD CELLULOSE FOR NITRATING IN PEACE TIME

In regard to the use of wood cellulose in peace times in the manufacture of smokeless powder, we have previously referred to the reluctance on the part of government officials to change from cotton to another form of cellulose, due to the serious question of chemical stability. In view of the enormous stocks of smokeless powder now in storage and the ample supply of cotton fiber for nitrating purposes, all smokeless powder for many years will continue to be made from cotton.

Relative to the use of wood pulp for industrial purposes other than explosives, there is a possible field. We believe that experiments in the past have in many cases failed because the investigator was satisfied to nitrate wood pulp as obtained from the paper trade and prepared for paper making purposes. We believe that better success can be obtained by giving the pulp an additional purification treatment so that the final cellulose will more closely approach cotton cellulose in chemical characteristics. This additional treatment naturally adds to the expense of the material.

Nitrocellulose prepared from wood pulp will be found to be of lower viscosity than cotton cellulose and might be of advantage for use in those industries where such a nitrocellulose is desired. As we have pointed out, however, there are serious difficulties in connection with the nitration of wood pulp alone, due to the physical character of the material and shortness of the fibers. These difficulties would of course have to be solved in order to make nitrocellulose from wood cellulose a serious competitor of nitrocellulose from cotton.

NEW CHEMISTRY BUILDING AT MONTANA STATE COLLEGE

The formal dedication of the new chemistry building of the Montana State College, at Bozeman, took place on January 14, 1920, in connection with the inauguration of Alfred Atkinson as president of the college.

The dedicatory address on "Chemistry in Our Agriculture and Mechanic Arts Colleges" was given by Prof. William F. Coover, head of the department of chemistry at the Iowa State College. Formal dedication was made by Chancellor Elliott, of the University of Montana.

Prof. E. A. Duddy, of the State College, outlined the history of the department of chemistry, which in 25 years has become one of the leading departments of the college. Its work began in 1894 in a frame building, used also as a skating rink, with a heating system which required the use of overshoes and overcoats in the classroom. Frequently from two to four classes recited in the room at once under different instructors.

NEW CHEMISTRY BUILDING, MONTANA STATE COLLEGE

Other addresses were made by President Atkinson of the State College, Director F. B. Linfield of the Montana Experiment Station, Dr. W. F. Cogswell of the State Board of Health, Prof. Lester J. Harzell of the Montana State School of Mines, Prof. W. G. Bateman of Montana University, Prof. C. C. Todd of Washington State College, W. H. Andrews, chemist for the Three Forks Portland Cement Co., Lyndall P. Davidson, chemist for the Anaconda Copper Mines' reduction department, and A. P. Stark, senior in chemistry at the college.

The new building, completed and equipped at a cost of $175,000, takes the place of one burned in 1916, and is believed to be one of the most up-to-date in the West. In many important features it is similar to the chemistry building at the Iowa State College.

It provides quarters for the department of chemistry and chemical engineering at the State College, research offices and laboratories for the Montana Experiment Station, water and food laboratories for the State Board of Health and an oil laboratory for the State Oil Commission.

The building has an efficient ventilating system for classrooms, offices, and laboratories, and a separate system for the laboratory hoods. The plumbing system provides pipe lines for hot and cold water, distilled water, drainage, compressed air, vacuum, and hydrogen sulfide. These pipe lines are placed in furred ceilings in each hallway and additional connections to all these lines can be made as future needs require. Alternate and direct current circuits are provided for each laboratory.

WILLIAM H. NICHOLS MEDAL AWARD

A unique situation was presented at the Chemists' Club, New York City, on the evening of March 5, 1920, in that the Nichols Medal for the first time was awarded to a previous recipient. For his brilliant paper on "The Arrangement of Electrons and Atoms in the Molecule," published in the June 1919 issue of the *Journal of the American Chemical Society*, Dr. Irving Langmuir was awarded the medal, following a unanimous vote by the jury of the award. Dr. William H. Nichols, the founder of the medal, made the presentation in a thoughtful address and in his usual felicitous manner. In his address of acceptance, Dr. Langmuir presented a general outline of the octet theory of valence. An unexpected feature was added to the evening by the exhibition of a series of models constructed by Mr. Leffert Lefferts illustrating the structure of molecules of well-known compounds according to the theory.—[EDITOR.]

MEDAL PRESENTATION

By William H. Nichols

GENERAL CHEMICAL CO.,
NEW YORK, N. Y.

The President of the SOCIETY regretfully finds himself unable to be with us to-night, and assume his privilege of presenting the SOCIETY'S medal to Dr. Langmuir. I have been asked to act in his place, and assume the honor with pleasure tinged with regret that our highest official should not be here to add dignity to the occasion. He has, however, written a most appreciative letter.

There are at least two points in which I can claim personal resemblance to Dr. Langmuir. We were both born in Brooklyn and we both, when we were rather young, attended public school, a course which I wish more American boys pursued. After that you know his history, where he was educated, the splendid work he did, and how, finally, after his graduation at Göttingen, he took up teaching at Stevens Institute. I am going to ask his permission and yours to take his career as a scientist for granted and to make use of an important decision of his, without in the slightest degree any criticism of it, to point a moral to what I consider one of the vital questions before the American people to-day. Dr. Langmuir began with teaching, and you can all imagine what kind of a teacher he must have made, and what kind of a teacher he would have grown to be, and you can therefore understand something of the great loss to this country which his giving up the teaching profession must have produced. Fortunately, he made good in other directions, and I do not doubt that his contribution to the world has been greater in the field which he has chosen than it would have been had he continued as a teacher of young men. But it frequently happens that such is not the case. I have seen men, young, splendid men, lured away from professional work into the industries, and I have seen them get smaller and smaller as time went on, and the output of the laboratory they abandoned dwindle as to quality because their places had been inadequately filled. Now you understand I am not saying these things in criticism of Dr. Langmuir, but I want to use the fact as a pretext to point out something which I consider of tremendous importance.

IRVING LANGMUIR, WILLIAM H. NICHOLS MEDALIST, 1919

We have had in this SOCIETY for several years a committee known as the Committee on Coöperation between the Universities and the Industries. The chairman of that Committee is now the President of the SOCIETY, and he has put a great deal of intelligent work into the operations of the Committee. I have been and am one of its members. I have been studying the work of that Committee, realizing, as all of us must realize, the absolute necessity, in one way or another, of getting a closer relationship between the universities and the industries. The lack of coöperation may possibly be likened to the invention of the sewing machine. You remember how difficult that was until some smart fellow happened to think that he could put the eye near the point of the needle. Then we had the sewing machine. Now this Committee has been working from below up with the idea of founding fellowships rather than providing for what the Fellows were to receive when they get to college. I have come to feel that it is more important to look out for the professor who is going to teach the Fellow, although fully appreciating the importance of the other point of view.

As you think of it thus, you see that the position of professor in the university or technical school (or for that matter, of teacher in all branches down to the primary school) has not in point of reward kept pace with the times; and the temptation which comes to a perfectly capable man to yield to the allurement of industry and leave his professorial work is strong, and his embracing the opportunity thus offered is by no means discreditable. Now the industries in holding out the lure cannot realize that they are "killing the goose that lays the golden egg." The case before us to-night is the antithesis of this, which shows that every rule has its exceptions. We must think of some way to make it to the interest of the best men in the profession to teach chemistry, or the science of chemistry will suffer here in comparison with other countries, and, as all of the industry of the country rests first upon the chemical industry and that in turn upon the chemist, this means that the effect will be shown in all of our industries if we do not find some way to induce the best men to remain. What is even more important is to induce the best men on graduating to prepare to fill the places which become vacant.

Now how can that be done? It is a problem of finance. Many of the colleges and universities have had, are having, or are going to have drives to make large and much needed additions to their endowment funds, and yet if they get all they ask there will not be enough in my judgment to carry out the idea which I have tried to express, of making the teaching of chemistry at our universities and colleges not only one of the most delightful employments, one of the most heartening and loving labors, which it is now, but also one of the most attractive from the point of view of the welfare of the incumbent himself as well as that of his family. This thought had led me to the conclusion that the relation between the universities and the industries must be shown in the readiness of the industries willingly, gladly, and from a sense, if you please, of enlightened selfishness, to see to it that the good chemical professors shall be adequately and even more than adequately provided for for the present, and also for the future by annuities for old age and insurance in case of death. I believe that this is the need, to take hold of the question from the professorial end, and not from that of the student alone. Of course, there will be an abundance of splendid students. How are they going to be met when they get to the college, and what kind of teaching are they to receive?

I think a plan is being devised, which is not yet advanced sufficiently to be made public, which will solve this question. I believe that before the year is out we shall see that this problem is in a fair way of solution, and that successful professors of chemistry will not only find themselves in one of the most delightful of all occupations, teaching, but that they will also be well paid. When that comes about we can all congratulate ourselves that our industries will continue to lead the world.

The gentleman who is to receive the SOCIETY's medal tonight is so well known to every one of you that words from me are unnecessary. This is not his first appearance. He received the medal in 1915. This will be his second recipiency and in this his case is so far unique. Moreover, the paper for which the Committee has awarded the medal had the distinction of being read twice at the same meeting. When at Buffalo it created such a sensation that he was asked to read it again, which he did. I do not recall another instance of this. It shows that instead of the vote of the Committee it was the vote of the SOCIETY; in fact, a real referendum.

Dr. Langmuir, in carrying out the very agreeable duty which is assigned to me, I do so with the utmost pleasure and with the right hand of fellowship. One of your qualities that we like, almost better than any other, is that you are always prepared to give credit to those who have been assisting you and to share with them the honor. It adds very much to my pleasure in presenting this medal to think that there are others who aided and assisted you in your splendid work, and that you generously make that claim in their behalf.

THE STRUCTURE OF ATOMS AND ITS BEARING ON CHEMICAL VALENCE

By Irving Langmuir

GENERAL ELECTRIC CO., SCHENECTADY, NEW YORK

According to the well-established Rutherford-Bohr theory, all the positive electricity in an atom is concentrated in a *nucleus* at its center. The dimensions of this nucleus are negligibly small compared with those of the rest of the atom, its diameter being of the order of 0.00001 of that of the atom. The charge on the nucleus is an integral multiple of the charge of an electron but of course opposite in sign. The remainder of the atom consists of electrons arranged in space about the nucleus, the normal number of such electrons (called the *atomic number*) being equal to the number of unit positive charges on the nucleus, so that the atom as a whole is electrically neutral. If the number of electrons in the atom exceeds the atomic number we have a negatively charged atom or ion while in the reverse case a positively charged atom or ion results. The atomic number of any element has been found to be equal to the ordinal number of the element in the periodic table. Thus hydrogen has the atomic number one, helium 2, lithium 3, carbon 6, neon 10, chlorine 17, nickel 28, silver 47, cerium 58, tungsten 74, radium 88, and uranium 92. The atomic numbers can be determined experimentally from the X-ray spectrum so that we are not dependent upon the periodic table for our knowledge of these numbers.

Bohr, Sommerfeld, and others have developed an extensive and very successful theory of spectra upon the hypothesis that the electrons in atoms are in rapid rotation in plane orbits about the nucleus in much the same way as the planets revolve around the sun. Stark, Parson, and G. N. Lewis on the other hand, starting from chemical evidence, have assumed that the electrons are stationary in position. It should be noted that Bohr's theory has had its greatest success when applied to atoms or ions containing only one electron and that it seems incapable of explaining the chemical or ordinary physical properties of even such simple elements as lithium, carbon, or neon.

The two theories can, however, be reconciled if we consider that the electrons, as a result of forces which they exert on one another, rotate about certain definite positions in the atom which are distributed symmetrically in three dimensions. Thus for atoms containing only a single electron the chemical theory is in agreement with Bohr's theory. But for an atom such as neon the eight electrons in the outside layer would revolve around positions which are located about the nucleus in the same way that the eight corners of a cube are arranged about the center of the cube. This structure is not inconsistent with those parts of Bohr's theory which have received experimental confirmation. In fact, Born and Landé,[1] starting from Bohr's theory and without knowledge of Lewis' work, arrived at exactly this conception of the structure of atoms (*i. e.*, the cubic atom) from a study of the compressibility of the salts of the alkali metals.

The atomic numbers and the properties of the inert gases furnish us with a clue to the arrangement of the electrons within atoms. The low boiling point, the high ionizing potential, the chemical inertness, etc., of helium prove that the arrangement of the electrons in the helium atom is more stable than that in any other atom. Since this atom contains two electrons we must conclude that a pair of electrons in the presence of a nucleus represents a very stable group. It is reasonable that with elements of higher atomic number there should be an even greater tendency for this stable pair of electrons to form about the nucleus. There are two sets of facts which furnish conclusive experimental evidence that this stable pair exists in all atoms above helium.

In the first place, the properties of lithium, beryllium, etc., show that in these elements also the first two electrons are held firmly while the remainder are easily detached. Thus, lithium readily forms a univalent positive ion by the detachment of one of the three electrons in its neutral atom. The divalence and other properties of beryllium prove that there is little or no tendency for a second stable pair of electrons to surround the first pair.

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[1] *Verh. d. phys. Ges.*, **20** (1918), 210.

In the second place, the absence of irregularities in the observed K and L series of the X-ray spectra of the various elements proves that there are no sudden changes in the number of electrons in the innermost layers of electrons about the nucleus. From these two sets of facts, as well as from other evidence, we may take it as a fundamental principle that the arrangement of the inner electrons undergoes no change as we pass from elements of smaller to those of higher atomic number.

The properties of neon indicate that its atoms are more stable than those of any other element except helium. Since the atomic number is 10, and the first 2 electrons form a stable pair about the nucleus as in the helium atom, it follows directly that the other eight electrons arrange themselves in a second layer or shell possessing a very high stability. If these 8 electrons revolved about the nucleus in a single circular orbit or ring, as would be suggested by Bohr's theory, there is no apparent reason why there should be any very great difference in stability between rings having 7, 8, or 9 electrons. On the other hand, we readily see that the geometrical symmetry of the arrangement of the 8 electrons at (or rotating about) the 8 corners of a cube would not only account for a high degree of stability but for the fact that an arrangement of 7 or 9 electrons would have no such stability. Chemical considerations and Born and Landé's work on compressibility also lead us to this spatial arrangement of the electrons. We shall refer to the stable group of 8 electrons by the term *octet*. From the principles already enunciated it is clear that in the atoms of all the elements above neon the inner electrons are arranged in the same way as those of neon.

From the atomic numbers of the inert gases we are thus able to determine the number of electrons in the various layers or shells of electrons which exist in the atoms. The results are summarized in Table I.

TABLE I—DISTRIBUTION OF ELECTRONS IN THE VARIOUS SHELLS

Shell	Number of Electrons	Inert Gas Corresponding to Completed Layer
1st shell	$2 = 2 \times 1^2$	He 2
2nd shell, 1st layer	$8 = 2 \times 2^2$	Ne 10
2nd shell, 2nd layer	$8 = 2 \times 2^2$	Ar 18
3rd shell, 1st layer	$18 = 2 \times 3^2$	Kr 36
3rd shell, 2nd layer	$18 = 2 \times 3^2$	Xe 54
4th shell, 1st layer	$32 = 2 \times 4^2$	Nt 86

Thus the xenon atom with an atomic number 54 contains 54 electrons arranged as follows: Close to the nucleus are two electrons which constitute the first shell. This is surrounded by the second shell which contains two "layers" of 8 electrons each. The third shell, which in the xenon atom is the outside shell, contains 18 electrons.

An examination of the numbers of electrons in the layers (Table I, 2nd column) shows that they bear a simple mathematical relation to each other, namely, that they are proportional to the squares of the successive integers 1, 2, 3, and 4. This is to be looked upon as perhaps the most fundamental fact underlying the periodic arrangement of the elements. It is significant that in Bohr's theory these same numbers, 1, 4, 9, 16, etc., play a prominent part. Thus the energies of the electron in the various "stationary states" are proportional to 1, $^1/_4$, $^1/_9$, $^1/_{16}$, etc., and the diameters of the various possible orbits in Bohr's theory are proportional to 1, 4, 9, 16, etc. In Bohr's theory the various stationary states correspond to different number of quanta (Planck's quantum theory), the innermost orbit corresponding to one quantum, the second orbit to two quanta, etc. We should thus consider (Table I) that the electrons in the 1st shell are monoquantic, those in both layers of the 2nd shell are diquantic, etc. It is interesting that Born and Landé from quite other evidence have concluded that the outermost electrons of the chlorine atom (2nd layer of the 2nd shell) are diquantic instead of triquantic as was at first assumed.

The foregoing theory of the arrangement of electrons in atoms explains the general features of the entire periodic system of the elements and is particularly successful in accounting for the position and the properties of the so-called 8th group and the rare earth elements. It also serves to correlate the magnetic properties of the elements.

Let us now consider the bearing of this theory of atomic structure on the phenomena of chemical valence. The outstanding feature of the theory is that there are certain groups of electrons, such as the pair in the first shell and the octet in the second, that have a remarkable stability. Those atoms in which all the electrons form parts of such stable groups (*viz.*, the inert gases) will have no tendency to change the arrangement of their electrons and will thus not undergo chemical change. Suppose, however, we bring together an atom of fluorine ($N = 9$)[1] and an atom of sodium ($N = 11$). Ten electrons are needed for the stable pair in the first shell and the octet in the second shell, as in the neon atom. The sodium atom has one more electron than is needed to give this stable structure while the fluorine atom has one electron too few. It is obvious then that the extra electron of the sodium atom should pass over *completely* to the fluorine atom. This leaves the sodium atom with a single positive charge while the fluorine becomes negatively charged. If the two charged atoms or ions[2] were alone in space they would be drawn together by the electrostatic force and would move as a unit and thus constitute a molecule. However, if other sodium and fluorine ions are brought into contact with the "molecule" they will be attracted as well as the first one was. There will result (at not too high temperature) a space lattice consisting of alternate positive and negative ions and the "molecule" of sodium fluoride will have disappeared. Now this is just the structure which we find experimentally for sodium fluoride by Bragg's method of X-ray crystal analysis. There are no bonds linking individual pairs of atoms together. The salt is an electrolytic conductor only in so far as its ions are free to move. In the molten condition or when dissolved in water, therefore, it becomes a good conductor.

The case of magnesium ($N = 12$) and oxygen ($N = 8$) is similar except that two electrons are transferred from the magnesium to the oxygen atom. The resulting ions have their electrons arranged exactly like those of the neon atoms and the ions of sodium and fluorine. Therefore, the crystalline form of magnesium oxide and sodium fluoride should be identical, and this prediction of the theory has been confirmed experimentally by Dr. A. W. Hull by the X-ray method. Because of the much greater forces acting between the ions as a result of the double charges, the stability of the magnesium oxide is much higher than that of the sodium fluoride. This is manifested by the high melting point, low conductivity, low solubility, and hardness of magnesium oxide.

Phosphorus ($N = 15$) and sulfur ($N = 16$) have, respectively, 5 and 6 electrons more than neon, and are thus capable of giving up these numbers of electrons. If these elements are brought into contact with an excess of fluorine (which because of its proximity to neon has a particularly strong tendency to take electrons) all the extra electrons pass to fluorine atoms. Thus a sulfur atom will supply electrons to 6 fluorine atoms and will form the compound SF_6. The force acting between the fluorine ions and the central sulfur ion is still electrostatic in nature but it must be nearly 6 times greater than the force between sodium and fluorine ions. Furthermore, the 6 fluorine ions would surround the sulfur ion so that there would be little stray field of force. Therefore, we should not expect sulfur fluoride to be salt-like in character but to consist of very stable molecules having weak external fields of force and, therefore, readily existing in the form of a gas. As a matter of fact this extraordinary substance has these properties developed to such a degree that it is an *odorless* and *tasteless* gas with a boiling point of —62°. Phosphorus pentafluoride, as would be expected from its less symmetrical structure, is a gas having greater chemical activity.

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[1] We will denote the atomic number of an element by N.

[2] It is convenient and it has been customary with many physicists to speak of a charged atom or molecule as an ion, irrespective of whether or not the particle is able to wander under the influence of an electric field. The writer has used the term in this way in his recent publications. This practice is very distasteful to many physical chemists and is apt to be misunderstood by them. Nevertheless, it seems to me probable, especially in view of the recent work of Milner and Ghosh, that it will be desirable to abandon the physical chemists' definition of the ion and to apply it to all charged atoms or molecules. The ion which wanders may then be referred to as a "free ion."

The fluosilicate ion SiF_6^{--} has a structure exactly like that of the sulfur fluoride molecule since the number and arrangement of the electrons are the same. This is clear if we consider that the atomic number of silicon is 14 while that of sulfur is 16. Thus if we should replace the nucleus of the sulfur atom in a molecule of sulfur fluoride by the nucleus of a silicon atom, without disturbing any of the surrounding electrons, we would have removed two positive charges and would obtain a negative ion with two negative charges of the formula SiF_6^{--}. In the presence of potassium ions we would then have the familiar salt potassium fluosilicate. The theory is thus capable of explaining typical complex salts. In fact, it is applicable to the whole field of inorganic compounds covered by the work of Werner, and helps to simplify the theory of such compounds. There is no time, however, to go into this subject.

The simple theory of atomic structure which we have discussed thus far explains perfectly what has usually been called "the maximum positive and negative valence." The maximum positive valence represents the number of electrons which the atom possesses in excess of the number needed to form one of the particularly stable configurations of electrons. On the other hand, the maximum negative valence is the number of electrons which the atom must take up in order to reach one of these stable configurations.

For example, magnesium has a positive valence of two, since its atomic number is 12 while that of neon is 10. Sulfur has a positive valence of 6 since it has 6 electrons more than neon; but it has a negative valence of two because it must take up two more electrons before it can assume a form like that of the argon atom.

It is clear, however, that this theory of valence is not yet complete.[1] It is not applicable to those cases where we have usually taken valences of 4 for sulfur, or 3 and 5 for chlorine, etc. But more especially it does not explain the structure of organic compounds and such substances as H_2, Cl_2, O_2, N_2H_4, PCl_3, etc.

J. J. Thomson, Stark, Bohr, and others had suggested that pairs of electrons held in common by two adjacent atoms may function in some cases as chemical bonds between the atoms, but this idea had not been combined with the conception of the stable groups of electrons or octets. G. N. Lewis, in an important paper in 1916, advanced the idea that the stable configurations of electrons in atom could share *pairs* of electrons with each other and he identified these pairs of electrons with the chemical bond of organic chemistry. This work of Lewis has been the basis and the inspiration of my work on valence and atomic structure.

As a result of the sharing of electrons between octets, the number of octets that can be formed from a given number of electrons is increased. For example, two fluorine atoms, each having seven electrons in its outside shell, would not be able to form octets at all except by sharing electrons. By sharing a single pair of electrons, however, two octets can be formed since two octets holding a pair in common require only 14 electrons. This is clear if we consider two cubes with electrons at each of the eight corners. When the cubes are placed so that an edge of one is in contact with an edge of the other a single pair of electrons at the ends of the common edge will take the place of four electrons in the original cubes. For each pair of electrons held in common between two octets there is a decrease of two in the total number of electrons needed to form the octets.

Let e represent the number of electrons in the outside shell of the atoms that combine to form a molecule. Let n be the number of octets that are formed from these e electrons, and let p be the number of pairs of electrons which the octets share with one another. Since every pair of electrons thus shared reduces by two the number of electrons required to form the molecule it follows that $e = 8n - 2p$ or

$$p = {}^1/_2(8n - e).$$

This simple equation tells us in each case how many pairs of electrons or chemical bonds must exist in any given molecule *between the octets formed*. Hydrogen nuclei, however, may attach themselves to pairs of electrons in the octets which are not already shared. For example, in the formation of hydrogen fluoride from a hydrogen atom and a fluorine atom there are 8 electrons in the shells ($e = 8$). We place $n - 1$ in the above equation and find $p = 0$. In other words, the fluorine atoms do not share electrons with each other. The hydrogen nucleus having given up its electron to the fluorine atom attaches itself to one of the pairs of electrons of the fluorine octet, and thus forms a molecule having a relatively weak external field of force. As a result, hydrogen fluoride is a liquid of low boiling point instead of being salt-like in character.

The equation given above is applicable to all types of compounds. For example, if we apply it to substances such as sodium fluoride, sulfur fluoride, or potassium fluosilicate, which were previously considered, we find in each case $p = 0$. In other words, there are no pairs of electrons holding the atoms of these compounds together. On the other hand if we consider the compound N_2H_4, we find $p = 1$. Since there are only two octets the pair of electrons must be between the two nitrogen atoms while the hydrogen nuclei attach themselves to pairs of electrons of the nitrogen octets. It can be readily shown that this simple theory is in fact identical with the accepted valence theory of organic chemistry and leads to the same structural formulas as the ordinary theory in all those cases where we can take the valence of nitrogen to be 3, oxygen and sulfur 2, chlorine and hydrogen one. In other cases such as those where quinquivalent nitrogen has been assumed, the new theory gives results different from the old but in each case in better agreement with the facts.

The theory indicates a series of new relationships between certain types of substances which I have termed *isosteric* substances. For example, it indicates that the molecules of carbon dioxide and nitrous oxide should have nearly identical structures and this is borne out by the extraordinary similarity in the physical properties of these gases. Nitrogen and carbon monoxide constitute another pair of gases which are similarly related. The same theory also points out a number of previously unsuspected cases of similarity of crystalline form (isomorphism).

It is clear that in the past the term valence has been used to cover what we may now recognize as three different types of valence, as follows:

1—Positive valence: the number of electrons an atom can give up.

2—Negative valence: the number of electrons an atom can take up.

3—Covalence: the number of pairs of electrons which an atom can share with its neighbors.

It is recommended that only for valences of the covalence type should definite bonds be indicated in chemical formulas. One of the particular advantages of the present theory is that it becomes easy to distinguish between covalence and the other types and thus to predict with certainty in what way electrolytic dissociation will occur if at all.

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[1] The theories of Kossel, Lacomblé, Teudt, etc., which have recently been proposed in Germany, have not advanced beyond this point and are therefore very unsatisfactory as a general theory of valence.

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FOREIGN INDUSTRIAL NEWS

By A. McMillan, 24 Westend Park St., Glasgow, Scotland

SYNTHETIC AMMONIA

According to *Comptes Rendus*, Professor D'Arsonval has made an important communication in the name of M. Georges Claude to the Academy of Science, Paris. M. Claude recently showed that it was not only possible, but very easy to produce and turn to industrial uses, pressures of 1,000 atmospheres and more. He has now succeeded in applying these pressures in the synthetic production of ammonia. Hitherto this has been done only in Germany, but M. Claude has surpassed the German scientists in that under the new conditions the combination of hydrogen and nitrogen takes place with such intensity that a very small apparatus is capable of a considerable output. He proposes shortly to show to the members of the Academy a tiny apparatus capable of producing daily 200 l. (44 gal.) of liquid ammonia. Whereas Haber could get only 0.33 g. of ammonia per catalytic gram, M. Claude gets 10 g.

ISOTOPES

An important communication, says the *Chemical News*, on the spectra of isotopic lead and thallium was brought before the Royal Society, London, by T. R. Merton. Interferometer measurements of the principal line in the spectra of ordinary lead and in lead from pitchblende showed that, in the latter case, the line was less refrangible by 0.0050Å., whereas the lead from Ceylon thorite was more refrangible by 0.0022Å. Thallium, which occurs in pitchblende in very small proportion, was examined by alloying it with pure cadmium and was found to give a line more refrangible than that of ordinary thallium by 0.0055Å.

MANGANESE IN BRAZIL

According to a report from the Bank (British) of South America, stocks of manganese ore continue to accumulate and as there is practically no demand for export, there appears to be little immediate likelihood of a demand occurring under peace conditions. The only solution likely to relieve this situation would seem to be the construction of suitable electric smelting apparatus for the reduction of the ore in Brazil. The stocks in hand at Rio de Janeiro on November 12 amounted to 256,279 tons.

ARTIFICIAL HONEY

During the war large quantities of artificial honey were used in Germany. The products of different firms did not show much uniformity, a thin fluid being much in evidence. According to an article in *Schweiz. Chem. Zeit.*, 1919, for the production of the thick variety, the water content and the degree of inversion of the cane sugar are matters of great importance. The water content must not exceed 22 per cent and the inversion must be complete to within 5 per cent. The inversion proceeds best when at least 0.1 per cent of formic acid is present. The strongly acid taste of the product is removed by neutralizing with sodium carbonate. On economic grounds, thick artificial honey is an indispensable product in Germany, and it is recommended that legislation be introduced to prevent confusion between natural and artificial honey.

METAL-MELTING FURNACE

A feature of the Alldays-Charlier metal-melting furnace is that no crucible is employed. It consists of a heavy steel-plate cylinder with cast-iron end plates, carried on two cast-iron standards provided with ball bearings. The cylinder is lined with refractory firebricks or cupola bricks, and the burner is arranged to play through one of the trunnions. The firing is by either oil or gas, and pouring is effected by tilting. As regards melting losses two sets of tests gave the following results: One set consisted of two tests made on gun-metal in the foundry of a large French factory. In one case the charge consisted of 541 lbs. of old copper, 99 lbs. of tin, and 20 lbs. of zinc, and the weight of metal poured was 645 lbs.; in the other the charge was 574 lbs. of old copper, 66 lbs. of tin and 20 lbs. zinc, and the poured weight 647 lbs. The melting loss was thus round about 2 per cent in both cases. Less favorable results were obtained by a foundry in the Haute Saône which specializes in "Parisien bronze." Old metal containing 65 per cent of copper and 35 per cent of zinc was melted; in one test the weight of the pour was 418 lbs. against 440 lbs. of charge, the melting loss being 5 per cent; while in the other 623 lbs. were poured from a charge of 660 lbs., the loss being 5.6 per cent. When the same metal was melted in an ordinary crucible furnace of the natural draught type the melting loss on a charge of 220 lbs. was 11 lbs. or 5 per cent. It is claimed, however, for the Charlier furnace that the elimination of expensive crucibles effects considerable economy and that its large production means reduced labor charges.

THE GREAT WAR EXHIBITION

According to *Engineering*, the Crystal Palace, London, will reopen in May next with the Great War Exhibition in which will be included a section relating to general and electrical engineering and another devoted to the petroleum industry. It is understood that the whole of the available space on the main floor of the building has been taken by the government for naval, military, and aircraft exhibits in connection with the war, but that some 50,000 sq. ft. of space are available for manufacturers wishing to exhibit in the engineering and electrical sections. The oil section will be accommodated in two large exhibition halls in the Palace grounds facing the terraces, one hall to be devoted to stand exhibits, and the other to machinery in motion. The special features of the oil section will be oil field supplies and general equipment, transport and distributing facilities, oil systems of power and domestic use, Diesel and other oil engines, exhibits by distributing and importing companies and government exhibits. All particulars of the exhibition, which will remain open till October, can be obtained from the General Manager, Crystal Palace, London.

ZINC-MANGANESE ALLOY

Among the new German alloys is one of zinc with not more than 4 per cent of manganese which is claimed to be about twice as hard as zinc itself and to have 50 per cent greater resistance to impact, while unlike other zinc it can be forged when warm as well as stamped and rolled. The alloy can serve as a substitute for copper, bronze, and brass.

THE MANUFACTURE OF GLUE

While the chemistry of gelatin, says *Nature*, **2623**, 611, has been investigated with much care, less attention has been given to that of glue. Both gelatin and glue are hydrolytic products of the collagen present in hides, but they represent different phases of the hydrolysis, and the details of the manufacture of glue have largely been kept secret. Crucial points are, first, the stage at which the process of hydrolysis must be stopped and the degree of concentration necessary in order to obtain a glue solution which will "set" to a jelly, and, next, the method of drying this jelly into a finished glue. A low temperature has been considered necessary for successful drying, and also for avoiding bacterial action during the process. Hence the making of glue in warm countries, such as India, has hitherto not been found practicable. A paper by Mr. K. C. Srinivasan, of the Department of Industries, Madras, on the "Manufacture of Glue in the Tropics," describes how the foregoing points have been investigated by the Department and the difficulties overcome. It is claimed that by a study of the chemical principles involved, and by laboratory and factory experiments, the details of manufacture have been successfully adapted to the climatic conditions prevailing even in the hottest parts of India.

SOURCE OF NITRATE OF AMMONIA

Prof. Garelli, of Turin, has lately been carrying out experiments with a view to the extraction of nitrate of ammonia from surplus stock of explosives. According to an article in *La Nature*, the explosive is allowed to stand with a fixed quantity of water in special vessels. A concentrated solution of nitrate of ammonia is thus formed and is separated by decantation. Powdered peat is then added to this solution and the product obtained after mixing and drying is a species of manure called "nitric peat." This material, which has the appearance of a blackish powder, gave the following analysis: Water, 17.8 per cent; ash, 18.8 per cent; nitrate of ammonia, 42.8 per cent; organic matter 20.6 per cent. Tests for ascertaining its value as a fertilizer have been carried out and the results show that its action is nearly equal to that of nitrate of soda.

ANHINGA

Anhinga, according to *Engineer*, **129**, 39, is a Brazilian plant which is chiefly found along the banks of the rivers of Para, whose slow current allows a soft mud bed for its roots. The plant constitutes a raw material from which cellulose for the manufacture of linen paper is obtained, and may also under chemical treatment be transformed into artificial cotton fiber. A new process for dissolving the fibers has been discovered which transforms them into very fine white fibers. These resemble cotton fiber of high quality but are considered to be superior to it inasmuch as the lines of the anhinga fiber are straight and parallel. It is said that the state of Para is capable of producing 100,000 tons of fiber for export annually and a mill already in operation has a daily output of about 10 cwt.

FUEL OILS IN SWEDEN

According to a report from Sweden, the Swedish Board of Trade has issued a report on the regulation of the market for imported fuel oils, and sulfite alcohol used as a motor fuel. The Board points out that the conditions for the distribution of liquid fuel are at present unfavorable, the chief inconvenience being that the Swedish fuel market is dependent on a small number of oil trusts. To remedy this evil, the Board recommends the acquisition by Sweden of foreign oil wells, the construction of a fleet of tank steamers of her own and the erection of oil refineries. For the transport of oil to Sweden two boats with an aggregate dead weight capacity of 12,000 tons are considered sufficient. The total cost of the two vessels is estimated at about Kr. 10,800,000.

TIN SOLDER SUBSTITUTES

In view of a continued shortage of tin in Germany, an article in the *Metallbörse* discusses the possibility of discovering suitable solder substitutes. During the war a considerable reduction in the proportion of tin in soft solders was permitted and such tin as was used was not taken from fresh ingots but from waste, ashes, and scrap. The proportion of tin varied between 25 and 40 per cent; that of lead was considerably increased and careless manufacturers often produced harmful results. Cadmium alloys, which, as a rule, are used only for very low smelted solders, came greatly into favor but such substitutes as this have no particular durability. Cadmium solder may be suitable in theory but is generally useless for practical purposes. The employment of solder substitutes in the gas meter industry has proved a failure, resulting in cracking on cooling, splitting on the slightest tension, and leaking in the seams of plates, etc. For dry gasometers antimony solder may be used with advantage but in other cases the employment of substitutes for tin has led to endless difficulties.

SULFUR IN BENZENE

According to a report in *Chemical Trade Journal*, **66** (1920), 200, the Aëronautical Inspection Department undertook investigations as to the effect of sulfur in benzene on various metals, at the request of the National Council of Commercial Motor Users and the Petroleum Executive. Four samples of benzene were supplied stated to contain 0.1, 0.2, 0.4, and 0.8 per cent of sulfur, respectively. Chemical investigation showed that sulfur was nearly all present as carbon disulfide. The metals used were copper, brass, phosphor bronze, aluminum, and cast iron. After prolonged contact with benzene containing 0.8 per cent sulfur, a slight discoloration of the surface took place in copper and brass. In the presence of moist air also, slight action appears to take place but no measurable difference occurred in the weights of the metal before and after the action. The iron and steel rusted in the moist air but there was no evidence of formation of any oxidation products of sulfur. A sample of the deposit found in carburetors of aëro-engines consisted of a grayish white powder decidedly alkaline to litmus and containing metallic particles. The particles consisted of aluminum with traces of copper, zinc, and iron. The remainder of the deposit was sodium silicate with traces of carbonate and sulfide, the latter probably impurities present in the sodium silicate used for doping the carburetors. There is, therefore, no evidence that the sulfur in benzene has any corrosive effect on carbureters.

ARTIFICIAL WOOL

According to the *Chemical Trade Journal* which quotes from a contemporary, considerable interest is being shown in Germany in a patent recently taken out on the manufacture of artificial wool. In principle the process consists of compressing wool scraps which cannot be otherwise utilized, shreds, ends, short fibers, and washing waste, and soaking them in a viscous solution of cellulose or one of its compounds with a small percentage of glue. The product thus obtained is cut into thin sheets or strips which can be treated after the manner of paper yarn. The Germans claim that the yarn thus obtained possesses all the properties of real wool. It is made waterproof by treating it in the process of manufacture with compounds of chromium and later with formaldehyde and tannin after which the product will resist the action of boiling water. The addition of glycerin gives it additional flexibility. The process is now being modified by the mixture with the woolen waste of a certain percentage of paper pulp, and treatment of the product with sulfuric acid and zinc chloride. The addition of various other compounds gives it the necessary flexibility and makes it waterproof.

NOTES AND CORRESPONDENCE

BRITISH NITROGEN PRODUCTS COMMITTEE REPORT

The final report of the Nitrogen Products Committee, Munitions Inventions Department, Ministry of Munitions of War of Great Britain, has been issued. It is a voluminous document of 323 pages with charts and tables covering several years' careful study of the nitrogen problem. It contains a summary of the pre-war position of the world's nitrogen industry, of the pre-war nitrogen industry of the United Kingdom; a discussion of power production and power requirements for nitrogen fixation; a study of costs and other economic features of established processes, and a discussion of partly developed processes, recent inventions, and research undertaken by the Nitrogen Products Committee and others. It goes into the effect of the war on the nitrogen industries and on future problems; depicts the post-war aspects of the nitrogen problem, and the post-war requirements of the United Kingdom. It also discusses the nitrogen resources of the United Kingdom and the establishment of nitrogen fixation in other parts of the British Empire. It closes with a summary of conclusions and general observations on nitrogen in agriculture; the world's demand and production; relative costs of synthetic and non-synthetic processes; the international situation after the war; and ends with a series of recommendations based essentially on provisions for the national safety of Great Britain, but also carefully considered from an industrial standpoint. Especial credit for this report is known to be due to Dr. J. A. Harker, director of the Nitrogen Research Section.

It is understood that these recommendations were made during the war period when it was advisable for England to develop every possible means for procuring nitrogen, exactly as was the case in the United States. The recommendations were confirmed by the Committee after the war was completed, as it seemed still desirable to have this information. Up to the present time, however, while the synthetic method is being developed, nothing has been done towards the development of a cyanamide plant in England, and it seems improbable that a cyanamide plant will be built in that country.

The recommendations of the Committee, under the chairmanship of H. E. F. Goold-Adams, are as follows:

RECOMMENDATIONS

In making the recommendations set out below, the Committee has been guided by the following salient facts:

(*a*) The sources of supply of combined nitrogen in the United Kingdom must be considerably increased if the existing and prospective home demands are to be met and the pre-war scale of exportation maintained.

(*b*) The existing sources of supply of combined nitrogen in the United Kingdom proved wholly inadequate for meeting the war demands.

(*c*) The risks and costs of importation during the war are very serious.

(*d*) Combined nitrogen (as cyanamide or ammonium sulfate) can be obtained by synthetic processes at a cost, at the factory, which is less than half the market price of combined nitrogen from other sources, pre-war conditions being taken as the basis in each case.

(*e*) Concentrated nitric acid can be made by synthetic processes for about half the pre-war cost by the standard retort process through Chile nitrate.

(*f*) The ammonia oxidation process provides a means whereby, during a state of war, the importation of Chile nitrate would be rendered unnecessary.

(*g*) The world's demand for combined nitrogen appears to double every ten years. The increased production during the war has not been more than the normal rate of increase during peace.

(*h*) The actual consumption of combined nitrogen for agriculture in the United Kingdom has practically doubled during the war, and there is certain to be a further increase.

(*i*) No very large increase in the output of by-product ammonia in Great Britain in the immediate future seems probable.

The following measures are recommended by the Committee as a minimum provision for safeguarding the future and for meeting a portion of the growing home demand for various nitrogen products.

CALCIUM CYANAMIDE PROCESS

The Committee recommends that this process should be established in Great Britain without delay, by private enterprise (supported, if necessary, by the government) or as a public work on a scale of manufacture sufficient to give an output of about 60,000 tons of cyanamide per annum, equivalent on the basis of combined nitrogen to about one-eighth of the present home production of ammonium sulfate. The necessary electrical energy should be obtained from water power in Scotland or from a large steam-power station, such as the capital power stations proposed by the Board of Trade Committee on Electric Power Supply.

On the basis of pre-war prices plus 50 per cent, the approximate capital outlay at a water-power site would be £1,680,000, inclusive of the capital cost of the hydro-electric development, the latter being taken at £40 per e. h. p. (£53.6 per kw.) of maximum demand. If the factory were erected at the site of a large steam-power station, the approximate outlay would be £800,000, inclusive of the proportionate cost of the power plant. The chemical sections for either site would cost about £445,000 of the above totals.

The approximate cost, at the factory, of raw cyanamide (19.5 per cent N) would be as follows:

Source of Power	Price of Electrical Energy per Kw. Year	Factory Costs per Metric Ton	
		Raw Product (19.5 Per cent N)	Combined Nitrogen as Raw Cyanamide
	£	£	£
Water	4	6.4	32.8
Steam (with coal at 11s. 3d. per ton)	5.6	7.0	36.0

The factory costs include interest on the capital outlay for the power section of the plant, but not on the chemical section, and are exclusive of any royalties.

The Committee suggests that it might prove desirable to arrange for a certain proportion of the calcium carbide produced to be utilized as such instead of converting it into cyanamide.

Plans and working drawings of the chemical sections can be obtained for a reasonable consideration. Moreover, as the result of the action taken upon the Committee's Interim Recommendations, considerable progress was made with the plans and specifications for a suitable steam-power station designed as the nucleus of a possible capital power station. These plans and specifications are available.

The Committee is authorized to state that the Board of Agriculture is of opinion that the establishment of this process would be beneficial.

SYNTHETIC AMMONIA (HABER) PROCESS

The Committee recommends that the synthetic ammonia process should be established forthwith on a commercial unit scale and extended as rapidly as possible, as a post-war measure, up to a minimum manufacturing scale of 10,000 tons of ammonia (equivalent to 40,000 tons of ammonium sulfate) per annum. The Billingham factory, begun by the government early in 1918 for the manufacture of synthetic ammonia and ammonium nitrate, should be completed and utilized for the purpose if such a course is practicable.

The evidence on the question of capital cost is somewhat uncertain, but the outlay for a factory of the capacity indicated, on the basis of pre-war prices plus 50 per cent, would probably amount to £600,000 if ammonia were the end-product, or to £780,000 if the factory were laid out for the manufacture of synthetic ammonium sulfate.

AMMONIA OXIDATION PROCESS

Early in the war, a full-scale installation was erected on the Thames by private enterprise, supported by the government, the older method of oxidation being utilized. A long series of experiments carried out at the Research Laboratory of the Department resulted in the design of a simple and modified plant which has been installed on a trial scale at several works in the country. The designs of the ammonia oxidation section of the government ammonium nitrate factory referred to above were based upon the results obtained in these research and trial operations.

The Committee recommends that an ammonia oxidation plant should be completed with the synthetic ammonia factory already referred to on a scale sufficient to produce about 10,000 tons of strong nitric acid (95 per cent) or its equivalent in nitrates, per annum; and that the plant should be designed to utilize *either* synthetic or by-product ammonia as a raw material.

Upon the basis of pre-war prices plus 50 per cent, the estimated capital outlay for an installation having a capacity of 10,000 tons of strong nitric acid (calculated as 100 per cent) per annum would be £120,000.

The process, when thoroughly tested, will probably lead to the ultimate abandonment of the older retort method of producing nitric acid from Chile nitrate, and also to the abandonment of niter pots in chamber sulfuric acid manufacture.

BY-PRODUCT AMMONIA INDUSTRIES

For conserving and increasing the output of combined nitrogen from existing by-product ammonia industries, for securing the better utilization of the national resources in coal, and for reducing the consumption of raw coal as a fuel, the committee recommends that:

(1) Encouragement should be given to facilitate and to ensure the replacement of non-recovery coke ovens by recovery ovens at a much more rapid rate than hitherto, in order that the reserves of coking coal shall be utilized to the maximum advantage.

(2) It should be made incumbent on all gas works which now contribute to the home supplies of ammonia nitrogen to put into practice the various simple expedients that have been proved to result in a considerable diminution in the loss of ammonia by volatilization or otherwise.

(3) In collaboration with the responsible organization of the gas industry, a comprehensive scheme of ammonia recovery and collection (including distribution of sulfuric acid) should be devised, which would be economically applicable to as many as possible of the smaller works where ammonia is at present allowed to run to waste. Wherever it can be shown that no financial loss would be incurred by any works included in the scheme, the works should be required to coöperate.

(4) In collaboration with the responsible organizations of the by-product ammonia industries, definite standards of efficiency in ammonia recovery should be formulated (based upon the qualities of coal in use and upon good average practice realized under the conditions in force at by-product recovery installations of various classes and sizes), and all works contributing towards the home supplies of ammonia should be required to conform to appropriate standards of recovery.

(5) Encouragement should be given to all efforts to extend the use of coal gas and coke in the place of raw coal for domestic purposes, for steam-raising, and for other industrial requirements.

TRIAL OPERATIONS AND RESEARCH

With regard to the trial in the United Kingdom of various nitrogen fixation and recovery processes, and to the general question of research upon the nitrogen problem, the Committee makes the following recommendations:

Hausser (or Explosion) Process

The Committee recommends that plans and estimates should be prepared for a plant of the smallest size sufficient for the thorough testing of the modified process by which nitric acid and power can be obtained simultaneously. In the events of the estimates proving favorable, a company possessing a coke-oven installation of the necessary capacity, or other suitable supply of gas, should be encouraged to erect the plant and carry out the trials.

Cyanide Processes

The barium process, using externally heated retorts, is at present under trial in this country.

The Committee recommends that steps should be taken to test, by means of a trial plant on a small works scale, other modifications of the processes, and especially internal electrical heating. The problem of devising a continuous process for the production of ammonia should be thoroughly investigated at the same plant.

Low Temperature Carbonization of Coal

This subject is under investigation by the Fuel Research Board.

The Committee recommends that any commercial plant erected or about to be erected in this country should be thoroughly tested. In the national interests, the trials should be organized and carried out by the government.

Sulfate Recovery Processes

The Committee recommends that the possibilities of sulfate recovery processes which avoid the use of sulfuric acid should be thoroughly investigated on a commercial scale, and encouragement and assistance should be given to companies and undertakings willing to carry out the trials for the benefit of the by-product ammonia industries as a whole.

Research

The Committee recommends that the researches on the nitrogen problem initiated during the war should be continued after the war under the auspices of the government for the general benefit of the country; and that the results of the researches carried out up to the present date should be edited and published at the earliest possible moment as a further Appendix to this Report, subject to such reservations as may be considered necessary by the government.

IMPERIAL SUPPLIES

The Committee recommends that a coördinated policy should be framed for safeguarding the future nitrogen requirements of the Empire, and this should be done by an Imperial Authority.

As the information already available concerning the future prospects and possibilities in the different portions of the Empire will need to be supplemented before such a policy can be framed, the Committee suggests that advisory bodies should be set up to examine the local aspects of the nitrogen problem and to furnish the Imperial Authority with the requisite data.

OTHER RECOMMENDATIONS

In connection with other aspects of the Committee's inquiry, the following additional matters arise:

Oxygen and Other By-Products from Nitrogen Plants

The Committee recommends that:

(1) All liquid air nitrogen plants used in connection with nitrogen fixation installations in the United Kingdom should be operated to the maximum advantage for supplying the growing home demand for oxygen and argon.

(2) The imposition of restrictive trade agreements—such as have been operative at nitrogen fixation installations abroad—which prevent the recovery and utilization of by-product oxygen from nitrogen plants, should not be permitted in this country.

STATISTICS

The Committee recommends that comprehensive annual statistics for the nitrogen industries of the United Kingdom and for the home consumption of coal by various classes of users and industries should be officially collected and a detailed summary of the figures published. Strong representations on this subject should be made to the government departments concerned. The Committee suggests that this question is also worthy of the attention of the overseas governments.

SPECIAL OBSERVATIONS

As far as the United Kingdom is concerned, nitrogen fixation and allied processes will constitute a new "key" industry. The Committee is of the opinion that the initiation and development of the industry will require the active support of the government.

HYGIENIC CONTROL OF THE ANILINE DYE INDUSTRY IN EUROPE[1]

The above is the title of a valuable report for the United States Department of Labor after inspection and study in an official capacity by one of America's ablest and most distinguished specialists in occupational diseases and hazards, Dr. Alice Hamilton.

The development of the coal-tar industries in the United States has carried with it the incident dangers, which were better recognized and more thoroughly controlled in Germany than in any other country. For obvious reasons this might have been suspected, but the fact was verified by inspection of works in England, France, Germany, and Switzerland. In drawing special attention to this subject it may be permitted to make reference to the need of an Institute for Industrial Hygiene in the United States.

In the words of Dr. Hamilton, "One of our difficulties in controlling occupational poisoning in American dye works has been our ignorance of the effects on the human body of the many substances which are encountered and we have had to depend on published reports from Germany and England to tell us where to look for danger and how to provide against it."

"The precautions taken in German plants are very elaborate—based on accidents which have actually occurred among workmen, or on careful animal experiments to determine the effects of a new substance." The Germans are in a position to give most valuable information for "even though they may no longer have any cases of poisoning, they can tell of their experience in earlier years when little was known about the effects of the new compounds till some workman or chemist had developed poisoning from them." The German was thus well versed in toxic substances long before he dishonored himself in breaking a solemn contract by using "poison gases" in warfare.

In this connection it may be stated that there is an urgent need for publication of an immense amount of valuable research carried on by the Chemical Warfare Service of the United States Army and Navy, which now appears to have little chance to reach the light of day. The data on the physiological factors and changes involved in fatigue also are of immense value.

While disclaiming an exhaustive treatment of the subject, Dr. Hamilton nevertheless considers in this brochure benzene, aniline, the nitrobenzenes and nitrotoluenes, chlorobenzenes, and various cyclic derivatives, among them the nitrated phenols, nitranilines, and phenylenediamines. Dimethylsulfate, phosgene, arsine, and the chromates are also considered.

Inhaled benzene vapors attack the centers in the central nervous system which control respiration, heart beat and heat production. Aniline workers develop bladder tumors. Many poisoned, by DNB, for example, appear outwardly as if very drunk. Dinitrochlorobenzene often delays its effect, with a slow onset of symptoms. Dermatitis comes from all nitro- and amino-derivatives of benzene. The above simply indicates a few of the numerous items of importance in the monograph.

Cleanliness of plant, ventilation, conditions for refreshment, and medical supervision are dealt with. Of these we have much yet to learn and more to put into practice. During the war the pressure drove existent plants to intense systems for super-production. The exigency of the situation brought about the hasty construction of many plants for the production of chemicals of great variety needed in the prosecution of the war. The speed factor did not admit providing all the preventives for the protection of the workers in some instances, and in others the transientness of contracts caused little concern for the welfare of labor. These and other factors associated with the enormous and permanent development of the chemical industry have caused thinking chemists to give the subject most serious consideration. In numerous instances every precaution known has been applied in American plants, yet there is a strong hope that something worth while might be done in a large constructive way to better conditions of labor in the industry.

There are plenty of good people in the chemical industries and there are farsighted corporations seeking means to improve the situation, but the evils of the conditions first serve to call attention to their existence. Efforts to palliate are evident in the provision of medical attention. It is good business to have healthy labor, but the motive is primarily humanitarian. Multiplication and adaptation of education for the workers call for teachers with qualifications peculiar to the needs.

The mephitic odor of the laboratory covers a maze of mystery in the lay mind and is held responsible for numerous maladies. The word "chemical" is sinister. Where chemical processes are in operation, especially when fumes or vapors, even though the latter be only steam, are seen to escape from the works, there grows a feeling of suspicion, often with reason, and all kinds of sickness are attributed to these "poisonous substances." If the writer may judge from numerous letters as well as his own experience in "fume matters," even the members of the medical profession are not free from these sensations. And well they may not be in many instances, for even though the action of many chemicals in varying degrees of concentration is known, the insidious effects of many more are absolutely closed books. They require most diligent study and painstaking research.

The program would call for the coöperation of the chemist, but not his direction. It calls for special training in the field of preventive medicine, which involves social welfare. An excellent, but limited, program of training given at a few institutions is available for those who seek, but the industries inform us that suitably trained men and women cannot be had in adequate numbers to meet the demands.

I speak without authority, but I assert with assurance that the chemical industry will welcome and coöperate with the separate efforts for the improvement of conditions. But it will go much further if those efforts be coördinated. So I venture to say that it would appear desirable to extend the present localized opportunities for instruction and tie them together in one main institute for research, advanced and special instruction, and for coördination.

Charles Baskerville, *Chairman*

Committee on Occupational Diseases
in the Chemical Trades, American
Chemical Society

College of the City of New York
New York, N. Y.
March 5, 1920

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[1] Monthly Labor Review (December 1919) of the Bureau of Labor Statistics, United States Department of Labor.

DIVISION OF INDUSTRIAL COÖPERATION AND RESEARCH OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY

As a result of the activity incident to raising its Eight Million Dollar Endowment Fund, the Massachusetts Institute of Technology has established a form of relationship with certain commercial organizations which bids fair to become an important factor in that much discussed and highly desired coöperation between educational institutions and the industries of the country. This relationship is set forth in a contract between individual industrial organizations and the Institute of Technology, under which the industry pays an annual retaining fee to the Institute, in return for which the Institute assumes certain definite obligations of such a character as it is clearly in a position to meet.

To execute the obligations thus incurred, the Institute has set up a separate organization known as the Division of Industrial Coöperation and Research. The adjective *industrial* limits the noun "coöperation" rather than "research," because the research work made possible by the new contract plan is not limited to industrial investigations. While originally the funds obtained under the contract were applied to the Endowment Fund of the Institute, those which accrue from contracts obtained since March 1 will be devoted to the support of the Division and to research, largely in fundamental science. This work will naturally be carried on largely at the Institute, but not necessarily so. The industrial progress of the community depends upon an active and productive interest in research everywhere, and it is the intention of the Division to support investigations of promise wherever found.

Obviously the most insistent demand which the industries make upon the universities is for men trained to solve the many problems with which these industries are confronted. Unfortunately many manufacturers in America still suffer from the erroneous idea, seldom met in Germany but very prevalent here, that only those men specifically trained in a definite industry can be of any help in promoting the progress of that industry. A soap manufacturer still asks for a man trained in soap-making; a tanner still seeks for a man who has had a "course in tanning." If a new factory is to be put into operation along old and well-tried lines, it is clearly to the advantage of the owner to obtain a man who can do well those things which have already been done by others. For this purpose, however, a man with factory experience and not a man who has just graduated from the university is indicated. If, however, it is desired to do better something which is already reasonably well done, the greatest promise lies not in the man who has spent his time while at the university in learning the specific details of this one industry, as these details were then known and practiced, but rather in a man whose whole time was spent in acquiring a sound knowledge of science and, so far as possible, a training in the application of science to existing problems, whatever the field in which those problems may have been found.

Hence the Institute does not agree to train men peculiarly fitted for any particular industry or to organize courses of study for the development of specialists. This special knowledge can best be obtained by working in that particular industry under a superintendent who knows well the technique of the industry. A year's factory experience in a well-administered plant will superimpose upon a man's scientific foundation a structure which will enable him not only to follow the old methods, but to determine the underlying reasons for their existence, and hence to form a rational plan for trying to improve on them. Someone has said that a practical man is one who continues to make the same old mistakes; a scientific man makes mistakes but they differ from time to time.

But for those industries which want to advance, something more must be done than to supply them a man with the regular four-year undergraduate course of study. The application of science and scientific method not only to the search for new knowledge and new processes but also to rational improvement of old processes is susceptible to organized effort, and is generally spoken of as "training for research." The method is the same whether the object be to establish some underlying principle or generalization without reference to its immediate application (pure science); or whether the problem be a search for knowledge concerning a definite reaction in order that the yield of a particular process may be thereby increased (applied science).

Some men work more enthusiastically on one type of problem and some on the other; and obviously the training can be as effective in one case as in the other. It is the quality and fundamental character of the work which counts, and not the interval of time which may be expected to elapse before the results may find utility.

The Division of Industrial Coöperation and Research will foster both types of investigation. The work in fundamental science will be supported by the retainer fees paid by contracting companies, while studies in applied science will be paid for by the contractor for whom the work is done; obviously, in the latter case the results obtained become the property of the contractor meeting the expenses of the investigations.

As previously stated, it is not the intention of the Division to limit its contractors to the facilities of the Institute. It has already been found advantageous to divert a large number of queries submitted under this plan to consulting engineers throughout the country, and it is expected that the practice will be greatly increased.

That wonderfully effective coöperation which in Germany was brought about by the interposition of governmental authority over both the universities and the industries must in America be effected by some such voluntary plan of mutual helpfulness as this contract provides. The Technology Plan will doubtless be improved upon as time goes on, but even to-day it has elements of great promise.

William H. Walker, *Director*
Division of Industrial Coöperation and Research

Massachusetts Institute of Technology
Cambridge, Mass., March 16, 1920

PURCHASE OF GERMAN BOOKS AND PERIODICALS

Editor of the Journal of Industrial and Engineering Chemistry:

It may be worth noting in the Journal that the Leipzig Book Dealers Association has agreed upon an arrangement whereby it is practically impossible to purchase German books and periodicals in any way that will even approximately take advantage of the current exchange rate of the German mark. A great many chemists have ordered German publications in the hope that in some way this could be done. How this works out may, however, be indicated by the following:

All German publishers now ask 100 per cent over the published price of all books and in addition to this the Leipzig Association adds 400 per cent for all publications for export (on January 15 this was 340 per cent). Furthermore they insist on payment at the rate of $9.00 per 100 Marks regardless of the current rate of exchange.

I have inquired into this carefully and I find that most of the importers are really getting a very small profit. The difficulty is at the other end. For example, a recent small book, publishers' price 20 Marks, actually sold to the American purchaser through a well-known New York importer for $4.00.

The working agreement of the Leipzig Association does not apply to secondhand books. It is possible for private individuals in Germany to purchase publications there at 100 per cent over the published price. No established dealer or importer will undertake to purchase books in this manner for American clients on account of the penalty of being excluded from all further purchases from any of the members of the German Publishers Association at Leipzig if discovered. A notice sent out by the Leipzig Association on January 15, 1920, states that government coöperation in this matter has been sought, but it is not clear that the government is actually a party to this arrangement. Certain German publishers and dealers bill their goods only in foreign money at substantially the equivalent of price increment agreed upon by the Leipzig Association.

A set of Liebig's *Annalen* advertised by a well-known German dealer at 14,000 Marks was sought by an American importer who cabled his Leipzig agent to purchase at this figure. In due time reply by letter was received to the effect that the price would be 21,000 Marks. A second cable to purchase brought the belated reply that the price would be 42,000 Marks, at which point negotiations were dropped.

This may give your readers some notion of the situation and indicate that the idea of purchasing German books at this time at a low figure on account of the exchange rate is largely a delusion.

25 West 43rd Street
New York, N. Y.
March 2, 1920

B. T. Brooks

CHEMICAL MARKET IN INDIA

Editor of the Journal of Industrial and Engineering Chemistry:

In one of your more recent issues, as I recall, you requested your readers to send in notes which might be of some interest to the rest of the subscribers to your magazine. It has recently fallen to my lot to purchase, or at least try to purchase, chemicals and chemical apparatus. The situation as I find it is that the country has but few houses supplying these things and, due to the war, low stocks. What we do get is Japanese and though these goods had a clear field they have failed utterly to capture the trade or gain the confidence of the Indian manufacturers and the buyers in the many colleges here. Just now supply houses are offering the remnants of their pre-war stocks of German goods, which are being bought in preference to Japanese goods. This is true of many kinds of buyers.

It occurs to me, therefore, that this country offers a peculiarly good place for American goods. I am constantly being asked the names of factories producing this or that thing of a chemical nature and it would seem to me that with the desire of the Indian purchaser to obtain American material some of our factories might well try to place their articles here. Thus far, needless to say, one cannot get an American chemical or piece of apparatus without importing it himself, but he can get and will be forced to accept German or other articles unless there is greater ease of purchase of American goods than at present. With the tremendous industrial development which India is making, and the far greater development which will be one of the not far-distant results of the war, this country will be a market worthy of some serious consideration.

I trust that this little note may be of some interest to the manufacturers at home. It is given for what it may be worth, but with the certain knowledge that the field is open and that American goods will receive a ready welcome here.

Lahore, India
January 12, 1920

Harold S. Bennett

CALIFORNIA INSTITUTE OF TECHNOLOGY

Throop College of Technology at Pasadena, California, has recently changed its name to the California Institute of Technology, in order to denote its transformation from a college of local significance to a scientific school of national scope. The institution has recently received two gifts of $200,000 each to form permanent endowments for the support of research in physics and chemistry, and a gift of $800,000 for general maintenance on condition that the new endowment be increased to a total of $2,000,000. Gifts totaling $280,000 have been received for the construction of new buildings, including an auditorium, physical and chemical laboratories, and a laboratory for aëronautical research.

CHANDLER LECTURE

The Chandler Lecture will be given on April 27 by Dr. Willis R. Whitney at Havemeyer Hall, Columbia University, on "The Littlest Things in Chemistry."

The Lectureship, which was inaugurated at the time of the celebration of the Fiftieth Anniversary of the founding of the School of Mines, in 1914, was allowed to lapse during the period of the war, and is now being reëstablished.

SQUALENE: A HIGHLY UNSATURATED HYDROCARBON IN SHARK LIVER OIL—CORRECTION

In the article of the above title [This Journal, 12 (1920), 63] the following correction should be made:

Page 71, 1st col., 19th line, "benzene" should be written "benzine."

Tokyo, Japan

Mitsumaru Tsujimoto

THE DETERMINATION OF CELLULOSE IN WOODS—CORRECTION

In my article under the above title [This Journal, 12 (1920), 264] the following correction should be made:

Page 267, 1st col., 12th line, "sufficient 3 per cent sodium hydroxide solution added" should read "sufficient 3 per cent sodium sulfite solution."

Berkeley, California

Walter H. Dore

SCIENTIFIC SOCIETIES

ALL READY FOR THE ST. LOUIS MEETING

Special Correspondence to the Journal of Industrial and Engineering Chemistry by John Walker Harrington

St. Louis, March 25—All signs indicate that the largest meeting of the American Chemical Society ever held will be that of the spring of 1920. If the enthusiasm and interest of the St. Louis Section can accomplish this alone that goal has already been reached. The St. Louisians never fail in anything which they undertake, and the members of this enterprising western Section of our Society represent the spirit of progress which has always characterized this city of leaders and pioneers.

That the members of the American Chemical Society will respond in legions to the invitation of our hosts of Missouri is shown by the many reservations which are being made at the hotels of the city. Arrangements have been made for special trains from neighboring centers, and it is expected that with the coming of April 12 there will be from two to three thousand chemists assembled for the sessions of the Society. Owing to the forethought of the Section in this city and of that of the University of Missouri, at Columbia, which joins with it as host, nothing has been omitted for making the stay of the visiting delegation an experience which they will remember with delight in years to come.

Charles E. Caspari

From a technical point of view, this Spring Meeting of 1920 promises to be an epoch-making one in this era of reconstruction. The fruits of victory have been gathered; the country is seeking to return to the norm of industry and commerce, and upon the chemists there rests especially the responsibility for bringing the activities of the nation back to their accustomed channels. In order that the chemical industry may do well its part in the national service, it is natural that it should consider well the matter of legislation. The address, therefore, of Mr. E. P. Costigan, of the Tariff Commission, will have a special bearing. Its subject, "Chemical Industry and Legislation," shows that Federal officials are considering very seriously the status of the chemical manufacture.

As shown by the program, the activities of the sessions begin to stir on the afternoon of Monday, April 12, when the Council Meeting will be held, and in the evening when the Council will be entertained at dinner at the University Club. When the visiting members assemble at the General Meeting in the Hotel Statler they will be officially welcomed by the Honorable Henry W. Kiel, mayor of St. Louis. The response will be given by Dr. W. A. Noyes, of the University of Illinois, the president of our Society. Following the speech of Mr. Costigan, the editor of the *Journal of Industrial and Engineering Chemistry* will speak of the responsibilities of chemistry in this important crisis of our national history.

Among the papers that will be delivered at the afternoon session of the General Meeting on the same day will be "The Prediction of Solubility," by J. H. Hildebrand; "Selenium Oxychloride, a Neglected Inorganic Solvent," by Victor Lenher; and "Studying Plant Distribution with Hydrogen Ion Indicators," by E. T. Wherry.

It is an index of the sturdy growth of the American Chemical Society that two new Sections will be formed at this meeting.

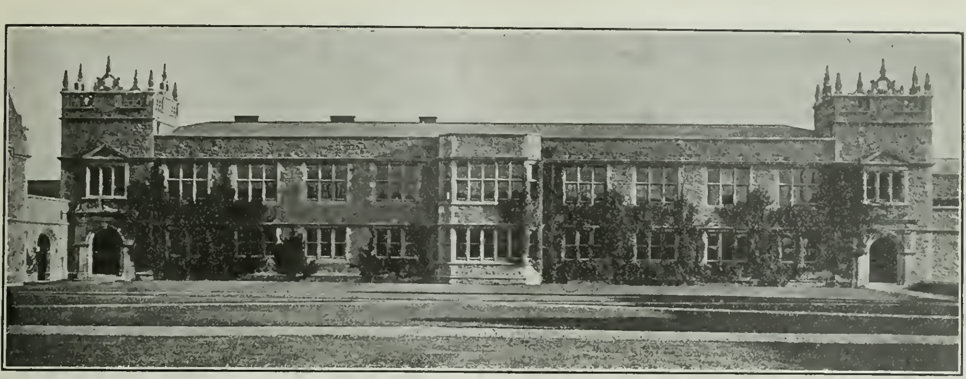
A Section of Leather Chemistry will come into being for the purpose of establishing a forum for the discussion of the chemistry of leather manufactures and other closely allied industries. No more appropriate place for founding so important a Section could have been selected than St. Louis, which by its traditions is an entrepôt of the cattle industry. In these days it is indeed a problem for mankind to find out how it shall be shod, and the new processes of tanning which the leather chemists are developing are destined to receive unusual attention. In the Organic Division the paper of Dr. John Arthur Wilson on "Vegetable Tanning as a Colloid Chemical Process" is also in line with the latest researches in the useful art honored by St. Crispin.

For the first time in the history of the Society a Section of Sugar Chemistry will meet; and it is also significant that it should be founded in this flourishing city which is within easy reach of the sugar-cane districts of the sunny South, as well as of the beet fields of Nebraska. There will be exhibited at the meeting of this Section the new American-made saccharimeter.

Those of us who were at Philadelphia will remember how the "Baby Section"—Dyes—burst out of its bright-hued swaddling clothes. It refused to take its assigned place in the Blue Room of the Bellevue-Stratford, nor would it be content either with the Green or the Red Room. Many did not believe that it would have more than 25 or 30, but when the veracious Secretary, Mr. R. Norris Shreve (the adjective is applied on account of his St. Louis birth), insisted that he could fill the Palm Garden, there were many doubters. The high count at the meeting of the Dye Section last year, however, was 385, and it is likely that this infant—which has now become a giant—will show an even larger growth next month and will be promoted to the rank of a Division. Many important papers in this Section have already been prepared.

Word comes from the office of the Secretary in Washington that there are also likely to be notable contributions from the Divisions of Agricultural and Food Chemistry, Biological Chemistry, Fertilizer Chemistry, Industrial and Engineering Chemistry, Organic Chemistry, Pharmaceutical Chemistry, and also in those Sections devoted to the Chemistry of Rubber and of Water, Sewage and Sanitation. The newspapers of St. Louis have already taken a deep interest in the approaching meeting, and have given liberal advance notices of it. On account of the many subjects of interest which will come before the various Sections, it is desirable that synopses of papers which have a popular appeal be sent as soon as possible to the A. C. S. News Service, care of the American Chemical Society, 35 East 41st Street, New York City, which, in coöperation with the Publicity Committee of our local Section and the St. Louis Convention and Publicity Committee, will use its best endeavors to see that full information is supplied to the press. In these synopses the relation of the subjects of the papers to every-day life or to the future of an industry should be stressed. Papers dealing with public policy, national affairs, the general welfare, food supply,

F. W. Frerichs



Busch Hall, Chemical Laboratory, Washington University, St. Louis

living and housing conditions, or with the announcement of discoveries and the results of original research, are always desirable in popular form. To insure their effective use for both the lay and technical press, they should be in hand not later than ten days in advance of the meeting.

The local committee is planning a series of excursions to the various chemical plants of St. Louis. This will give all the members an ample opportunity for seeing the leading drug center of the West, which leads the country in the production of synthetic pharmaceuticals, alkaloids, and anesthetics. This also is an important center for ceramics, glass, paint, lead, and zinc. These last two important metals are mined not very far from the city in whose industries they are notable factors. Among the plants to be visited are those of the Laclede By-Products Coke Company, the Monsanto Chemical Works, the Laclede-Christy Clay Products Company, the Standard Oil Company Refinery at Wood River, Illinois, and the Illinois Glass Company at Alton, Illinois.

The social features of the St. Louis meeting are eloquent of the spirit of hospitality which characterizes this city. On the evening of April 13 there will be a theater party for the ladies, and at the Liederkranz Club a smoker for men. Several automobile tours have also been planned.

Washington University grouped about its stately quadrangle waits to welcome the Knights of the Retort. Dr. Ball, of its department of chemistry, will officially keep the census of the Spring Meeting. He was discovered to-day blending the ingredients of a new adhesive which will keep delegates attached to one place until they have been duly registered and badged. He and Dr. L. McMaster, former chairman of the St. Louis Section, are busy in the well-equipped laboratories of the institution training ambitious youth, and let us hope future members of the A. C. S. Their students include some of the gentler of the species which shows there is a chemical career for woman in the ever-progressive State of Missouri. There is no more beautiful region in all the academic world than the campus and the neighboring Forest Park in which the fine old University is set like a jewel. It is in sight also of the Museum of Art, the Jefferson Memorial, and other structures which adorn this wonder city of Laclede. Your correspondent to-day, making an automobile tour of the metropolis of the West through the kindly invitation of Dr. Nickell, saw many signs of the charm which comes to the valley of the Mississippi when Mother April makes all things new. They were pledges of the time when the parks and the famous Shaw Botanical Garden will surpass Kew at its best. It is well worth crossing the continent to be here in April and, as most of us, owing to the central position of St. Louis, will not have to go more than half as far, to miss this Spring Meeting would be to let slip an alembic of good fortune.

The local committees in charge of the arrangements for the St. Louis meeting are: Edward Mallinckrodt, Sr., Honorary Chairman, Executive Committee; Charles E. Caspari, Chairman, Executive Committee; F. W. Frerichs, Chairman, Finance Committee; L. F. Nickell, Chairman, Publicity Committee; Gaston DuBois, Chairman, Excursion Committee; H. A. Carlton, Chairman, Hotels Committee; T. R. Ball, Chairman, Registration and Information Committee; A. C. Boylston, Chairman, Transportation Committee; E. J. Sheppard, Chairman, Banquet Committee; F. W. Sultan, Chairman, Smoker Committee; and Mrs. C. E. Caspari, Chairman, Ladies' Entertainment Committee. These committees are assisted by: F. W. Russe, P. A. Shaffer, Herman Schlundt, Edward Mallinckrodt, Jr., Jules Bebie, B. M. Duggar, H. M. Whelpley, J. W. Marden, P. C. Brooks, E. R. Cramer, J. M. Olin, R. S. Sherwin, A. D. Alt, George Lang, Jr., J. T. Ragsdale, Jr., O. H. Pierce, D. B. Conrad, E. R. Harding, A. W. Becker, W. E. Buck, H. E. Wiedemann, F. B. Langreck, W. R. Teeters, R. R. Barlow, L. J. Chamberlain, J. D. Robertson, L. McMaster C. C. Luedeking, Hamilton Merrill, W. F. Monfort, W. S. Ritchey, and F. E. Turin of the St. Louis Convention and Publicity Bureau.

AMERICAN PHARMACEUTICAL ASSOCIATION

During the Annual Convention of the American Pharmaceutical Association, to be held in Washington, D. C., on May 4 to 10, 1920, the Scientific Section will hold its meetings on Thursday, Friday, and Saturday, May 6, 7, and 8. Those desiring to read papers before this section should submit them to the Secretary, Dr. A. G. DuMez, Hygienic Laboratory, U. S. Public Health Service, Washington, D. C., not later than April 1.

AMERICAN ELECTROCHEMICAL SOCIETY

The Spring Meeting of the American Electrochemical Society will be held in Boston, Mass., April 8, 9, and 10, 1920, and promises to be unusually attractive and interesting.

The annual business meeting, at the Massachusetts Institute of Technology on April 8, will be followed by the address of the retiring president, W. D. Bancroft, on "Contact Catalysis," a symposium on "Colloids," and other interesting papers. The evening will be occupied by a smoker.

The meetings on April 9 will be joint sessions with the American Institute of Electrical Engineers.

There will be an excursion to the General Electric Plant at Lynn on Friday afternoon, April 9, and to the Huff Electrostatic Separator Company on Saturday afternoon, April 10.

PROGRAM OF PAPERS

A Criticism of Kohlrausch's Law of the Conductivity of Solutions. Guy Clinton.
Hydrogen Ion Concentration in Dry Cells. H. D. Holler and L. M. Ritchie.
The Reactions of the Lead Accumulator. D. A. McInnes.
Arc Images in the Chemical Analysis. Wm Roy Mott.
The Soderberg Self-baking Continuous Electrode. J. W. Richards
Synthetic Electric Furnace Pig Iron. Chas. A. Jeller.
Step Induction Regulators for Electric Furnaces. Philip B. Short.
The Electric Furnace as Applied to Metallurgy. Clarence J. West.
The Electric Brass Furnace, Its Evolution. H. M. St. John.
The Electric Furnace in Iron and Steel Metallurgy. L. B. Lindemuth.
Reduction of Manganiferous Silicate Slags. Edw. F. Kern.

Symposium: Colloid Chemistry

Colloid Chemistry and Electrochemistry. W. D. Bancroft.
Settling Problems. W. A. Deane.
The Adsorption of Arsenious Oxide by Metastannic Acid and the Purification of Spent Electrolyte. T. R. Briggs and W. J. Bartlett.
Grafitic Acid, a Colloidal Oxide of Carbon. G. A. Hulett.
Determination of Grafitic Carbon. A. C. Fieldner
Selective Adsorption by *Bacillus pyocyaneus*. Wm. C. Moore.

Symposium: Electrically Produced Alloys

W. D. Bancroft, *Presiding*

Fundamental Problems in Alloys Research. H. E. Howe.
Recent Developments in the Ferro-Alloy Industry. R. J. Anderson.
The Manufacture of Ferro-Alloys in the Electric Furnace. C. B. Gibson.
Ferrovanadium. B. D. Saklatwalla.
Stellite. Ellwood Haynes.
Properties of Ferrosilicon. F. A. Raven.
Ferromanganese. E. S. Bardwell.
The Manufacture of High Speed Steel in the Electric Furnace. R. C. McKenna.
Ferrocerium. Alcan Hirsch.
Ferrozirconium. Theodore Swann.
Ferrophosphorus. B. G. Klugh.
Nichrome and Other Special Alloys. R. M. Major.
Electric Properties of Nickel Iron Alloys. T. D. Yensen.
Electrical Properties of Titanium Alloys. M. A. Hunter.
Nitrogen Fixation by the Silent Discharge. C. F. Harding.

Symposium: Power for Electrochemical Industries

President C. Townley, of the A. I. E. E., *Presiding*

Power for Electrochemical Plants. John L. Harper.
Automatic Control of Arc Furnace Electrodes. John A. Seede.
Reactors for Electric Furnace Circuits. H. A. Winne.
Economies of the Power Situation. C. A. Winder.
Electric Furnace Power from the Standpoint of the Central Station. E. A. Wilcox.
The Electric Furnace and the Central Station. H. L. Hess.
Location of a New England Electrochemical Plant. C. T. Maynard.
Water Powers of the Pacific Coast. F. F. Fowler.
Power Development in Scandinavia. J. W. Beckman.
Power Problems from the Standpoint of the Furnace Operator. W. G. Berlin.

CALENDAR OF MEETINGS

American Electrochemical Society—Spring Meeting, Boston, Mass, April 8 to 10, 1920.

American Drug Manufacturers' Association—Annual Meeting, Hotel Biltmore, New York, N. Y., April 12 to 15, 1920.

Technical Association of the Pulp and Paper Industry—Spring Meeting, Hotel Waldorf and Hotel Astor, New York, N. Y., April 12 to 16, 1920.

American Pharmaceutical Association—Annual Convention, Washington, D. C., May 6 to 8, 1920.

American Chemical Society—Fifty-ninth Meeting, Hotel Statler, St. Louis, Mo., April 12 to 17, 1920.

National Foreign Trade Council—Convention, San Francisco, Cal., May 12 to 15, 1920.

National Fertilizer Association—27th Annual Convention, White Sulphur Springs, W. Va., week of June 21, 1920.

American Institute of Chemical Engineers—Semi-Annual Meeting, Montreal, June 21 and 22; Ottawa, June 23; Shawinigan, June 24 and 25; La Tuque, June 26, 1920.

WASHINGTON LETTER

By J. B. McDonnell, Union Trust Building, Washington, D. C.

Efforts to have the embargo section of the Longworth dye bill eliminated when that measure is again called up in the Senate for consideration will be made by opponents of the bill.

The bill was called up in the Senate and debated for a day just before the Treaty of Peace was again taken up. No action was taken on the bill, however, a small filibuster staged by western senators as a means of forcing the Senate Finance Committee to act on other tariff measures pending before it preventing any final action. Following its action in reporting favorably the dye bill, Republican members of the Senate Finance Committee determined to "smother" in committee the other tariff measures which had been passed by the House, including the surgical and scientific instruments bill, the magnesite, zinc, and pearl button bills.

The committee conclusion met with strong opposition from western senators in whose states were located the interests affected by the bills it had been determined to smother, and when the dye bill was taken up on the Senate floor they were open in their condemnation of the committee's procedure, and the dye bill was debated for the day without any action being taken. The calling up of the Peace Treaty the next day under agreement has prevented further consideration of it up to this time.

Responding to the urging of textile interests of New Hampshire, Senator Moses of that state has introduced an amendment to the committee bill which would eliminate the embargo section entirely. In its stead it would permit all dyes to be imported under the duties assessed in the tariff section of the committee bill, plus a duty sufficient to make the price of the imported dye equal to the "fair wholesale price" of the same dye when manufactured in this country.

The fair wholesale price, the bill states, means the "lowest wholesale price sufficient to insure the maintenance in the United States of the production of such article by an efficient plant operated on a scale reasonably adequate to supply ordinary domestic demands." This price is to be determined by the Secretary of the Treasury.

The Moses amendment, which is pretty much an anti-dumping measure, would assess duties as follows:

> (*b*) In addition to the duties provided in Section 500 of this Act, there shall be levied, collected, and paid, during the period of three years beginning from the date of the enactment of this amendatory Act, upon any article enumerated in Group II or Group III of such section, if at the time of importation of such article a like article or a satisfactory substitute therefor is manufactured and offered for sale in the United States on a substantial commercial scale, an additional duty equal to the difference between (1) the sum of the dutiable value of such article, ascertained as provided in subdivision (R) of Section III of the Act entitled "An Act to reduce tariff duties and to provide revenue for the Government, and for other purposes," approved October 3, 1913, plus all non-dutiable costs, charges, and expenses incident to the importation thereof, and any duty thereon imposed by Section 500 of this Act, and (2) the fair wholesale selling price in the United States of a like article or satisfactory substitute therefor of domestic manufacture, plus 20 per centum of such wholesale selling price in the United States: Provided that subdivision (2) exceeds subdivision (1).

The amendment goes on to prohibit false labeling and provides penalties for incorrectly labeled dyes brought into this country.

Senator Moses has expressed the belief that in spite of the confidence expressed by supporters of the committee measure, it will meet with considerable opposition when called up on the floor again, and declared that Senators Dial, Keyes, Henderson, Pittman, Sherman, Poindexter, himself, and some others, are opposed to the committee bill. Senator Keyes, it is said, intends to offer several amendments.

With Republican and Democratic leaders supporting the committee bill, Senator Watson, of Indiana, in charge of the measure, is confident of its passage without material amendment. When it will be called up again depends upon the course of the treaty debate. It is planned to bring the dye bill up as soon as the treaty is disposed of.

Acting against commercial bribery practiced by dealers in dyestuffs and chemicals, the Federal Trade Commission has issued complaints against 22 concerns. In ten cases the commission has issued a report, dismissing one complaint—that against the Commonwealth Color & Chemical Company, of New York—and issuing orders to "cease and desist" from commercial bribery against the other nine concerns whose cases have been tried. The concerns named in complaints issued by the Federal Trade Commission are F. E. Atteaux & Company; Dearborn Chemical Company; The Commonwealth Color and Chemical Company, and Herbert L. Wittnebel, a salesman of that concern; the Federal Color & Chemical Co.; William Mohrmann; John Campbell & Co.; Holliday-Kemp Co., Inc.; A. Klipstein & Company; Geigy Company, Inc.; C. Bischoff & Company, Inc.; The Heller & Merz Company; The Franklin Import & Export Company, Inc.; New York Color & Chemical Company; Louis Rosenthal, doing business under the name and style of the United Chemical & Color Company; Andreykovicz & Dunk, Inc.; Arkansas Distributing Company; Pennsylvania Salt Manufacturing Co.; L. Richardson, H. Smith Richardson and L. Richardson, Jr., co-partners, doing business under the name of The Vick Chemical Company; The Arabol Manufacturing Co.; Bosson & Lane; and Ricco Company, Inc.

All of the concerns named in the complaints issued by the Commission are accused of giving gratuities "consisting of cigars, meals, drinks, entertainment and in some instances small presents," while several of them are also accused of giving and offering to give to employees of both customers and prospective customers and competitor's customers "sums of money." With the commercial bribery in mind, with which the dyestuff and chemical business in this country was infested prior to the war, it is not surprising that a number of dealers are yet to be found who cling to the methods which in the past have been so effective as one of the means used to prevent the development of a real dye industry here. It is interesting to note, however, that none of the larger American manufacturers of dyestuffs or chemicals have been included among those against whom complaints have been issued by the Commission.

Concerns against which the Commission found its complaint to be justified and issued orders to cease and desist include F. E. Atteaux & Co., Inc.; Federal Color & Chemical Company; William Mohrmann; John Campbell & Company; Holliday-Kemp Company, Inc.; A. Klipstein & Company; Geigy Company, Inc.; C. Bischoff & Co., Inc.; and The Arabol Manufacturing Company.

While the Senate has been debating the Treaty, after having taken it up once more for consideration, the House has latterly been engaged in consideration of the army reorganization measure. As did the new army bill reported by the Senate military committee, the House bill provides for a separate Chemical Warfare Service. Prominent members of the House, however, consider the bill defective in that it does not define the dutes of the Chemical Warfare Service, and therefore the General Staff, which has openly opposed a separate Chemical Warfare Service, would be enabled practically to kill the Service if it so desired. Representative Dent has announced that he will seek to guard this point in the legislation. The action of the House committee in making this Service a separate department of the Army was early forecast. There seems little doubt but that the House will sustain the committee and that when the army reorganization is finally worked out the importance of chemistry, not only in peace, but in warfare also, will have been recognized by both House and Senate, and the Chemical Warfare Service set up as a separate and distinct department of the Army. Any other action would be surprising to those in charge of the measures in both bodies.

It is interesting to note in this connection that Major General William L. Sibert, who had been chief of the Chemical Warfare Section of the Army, has been replaced by Lt.-Col. Amos Fries. Colonel Fries was put in charge of the Chemical Warfare Service of the American Expeditionary Forces and served in that capacity in Europe until the end of hostilities. Upon his return to this country he resumed his former rank and was recently put in charge of the Service in this country.

Dr. S. W. Stratton, chief of the Bureau of Standards of the Department of Commerce, appeared before the Senate Appropriations committee recently and urged that the Senate reverse the action of the House in reducing the appropriations asked for by the Bureau to carry out its important work. Like many other departments and bureaus, the Bureau of Standards was struck by the program of economy determined upon by the Republicans in Congress, and its appropriations for the ensuing year were cut even below the sums granted in the last appropriation bill for the current year. The importance of the work of the Bureau was emphasized to the committee by Dr. Stratton, who asked that the Senate at least restore the appropriation to the amount granted this year.

March 15, 1920

OBITUARIES

FRANCIS C. PHILLIPS

Dr. Francis Clifford Phillips died at his residence, 144 Ridge Ave., Ben Avon, Pa., on Monday, February 16, 1920, of influenza-pneumonia, passing away in the same peaceful manner which characterized his life.

Francis C. Phillips

He was born in Philadelphia, April 2, 1850, the son of William S. and Fredericka Ingersoll Phillips. He received his early education at home from an unusually capable and devoted mother. In 1864 Dr. Phillips studied at the Academy of the Protestant Episcopal Church in Philadelphia, and in 1866 entered the University of Pennsylvania, where he obtained his A.B. From 1871–1873 he studied under Regimus Fresenius at Wiesbaden, Germany. During the latter year he was private assistant to Prof. Fresenius. He then spent a year at the Polytechnic School at Aachen (Aix-la-Chapelle). Here he was associated with Prof. Landolt. Professor Phillips was unable to complete his studies abroad because of the poor health of his father. He returned to America, and during the following year became instructor in chemistry at Delaware College. In 1875 he was appointed to the teaching staff of the University of Pittsburgh, then the Western University of Pennsylvania, where he taught for forty years, retiring as head of the department in 1915. For many years he taught chemistry, geology, and mineralogy. In 1878–1879 he also lectured to the students in the Pittsburgh College of Pharmacy. In 1879 he received the degree of A.M. from the University of Pennsylvania, and in 1893 the Ph.D. from the same institution. In June 1919 Dr. Phillips received the honorary degree of Doctor of Science from the University of Pittsburgh.

He was married in 1881 to Sarah Ormsby Phillips, daughter of Ormsby Phillips, a former mayor of Allegheny.

In 1915 Dr. Phillips retired from active service in the University of Pittsburgh under the pension system of the Carnegie Foundation. On this occasion his colleagues and the alumni tendered him a banquet at which he was presented with a check for one thousand dollars for a little vacation with "Mother" Phillips. Professor Phillips was so solicitous of the safety of his dear wife, that though they intended visiting the Bermudas and the Panama Canal Zone, the war, with the possible accompanying danger in ocean travel, caused him to postpone the trip which was never realized. At the banquet, the fruit of his labors as a teacher was in plentiful evidence, including such men of prominence as George H. Clapp, J. M. Camp, Walther Riddle, C. M. Johnson, Charles Kellar, Charles Dinkey, W. A. Hamor, Jacob Rosenbloom, the late Robert Carnahan and many others. It was an evening of tribute to one who had so conscientiously given to former students all that he possessed as a teacher

Since 1915 he had been engaged continuously in research and writing in a laboratory provided by the Mellon Institute.

During the recent war he conducted researches on gases in coöperation with the Gas Warfare Service.

Dr. Phillips was an authority on natural gas, in which field he held international recognition. In 1904 he published the "Methods of Analysis of Ores, Pig Iron and Steel Used by the Chemists in the Pittsburgh Region," and in 1913 a "Textbook of Chemical German," of which a second edition appeared in 1916. At the time of his death Dr. Phillips had two other books well under way, one on the "Life and Work of Joseph Priestley," the other on "Qualitative Gas Reactions."

Dr. Phillips was a member of the following societies:

Phi Kappa Sigma Fraternity since 1867.
Engineers' Society of Western Pennsylvania since 1880.
American Association for Advancement of Science since 1887.
American Institute of Mining Engineers since 1892.
American Chemical Society since 1894
American Philosophical Society since 1894
Phi Lambda Upsilon Fraternity since 1919.

Dr. Phillips was a member of the Chemists' Club of New York City and the University Club of Pittsburgh. He had been a member of the Council of the American Chemical Society since the organization of the Pittsburgh Section in 1903.

As the Rev. Henry H. Forsythe so aptly said at the funeral service, Professor Phillips' life was characterized by many great virtues. Though recognized throughout the world for his researches on gases, he was simple and plain as a child and never refused another his counsel on any matter. He possessed a modesty rarely seen in men and walked always in a humble spirit. He loved and bore the love of his many pupils, who though they might have had a difference in the classroom invariably learned to love the dear professor. He was the gentlest and kindest of men. As in his scientific researches he realized that the strictest observance of truth and honesty was necessary for the accurate solution of nature's secrets, so in life he walked uprightly and knew not of untruth or subterfuge.

Beside his widow, Mrs. Sarah Ormsby Phillips, Dr. Phillips leaves two sons, Clifford S. and Frederick I. Phillips.

Alexander Silverman

DAVID SHEPARD PRATT

The sudden death of Dr. David Shepard Pratt, on January 28, 1920, was a distressful misfortune to the world of science. While his published researches in the field of organic chemistry had been looked upon as achievements and had accordingly directed attention to his rare ability as an investigator, yet some of his most important accomplishments—some of those which had resulted from his contact with industry—were still awaiting preparation for publication at his hands, and at the time he succumbed to pneumonia he had just finished the development of several processes of undoubted value to agriculture. His end was very premature, and it is with an acute sense of bereavement that this occasion is taken to pay a brief word of tribute to so esteemed and efficient an associate.

David Shepard Pratt, son of Charles Manville and Louise Hale (Woodford) Pratt, was born at Towanda, Pa., on September 20, 1885. He was graduated at Cornell University with the degree of A.B. in 1908, and remained there as a Fellow in Chemistry until 1911, when he received the degree of Ph.D. He then joined the staff of the Bureau of Chemistry in Washington, D. C., as assistant chemist, but remained there only a short time, being soon selected as Chief of the Organic Division of the Bureau of Science in Manila, P. I. His chemico-economic studies in the Philippines were varied and valued, and he also acted as a member of the Pure Food and Drug Board. In 1914 he returned to the States to accept a professorship of chemistry at the University of Pittsburgh, and he successfully occupied that chair and the headship of the organic department of the School of Chemistry for three years—until he was made an Assistant Director of the Mellon Institute of Industrial Research. On January 1, 1920, after three years' service, he resigned at the Institute and was arranging to enter consulting chemical practice in St. Louis, Mo., at the time of his fatal illness.

From his student days at Ithaca, Pratt's studies in organic chemistry were characterized on the one hand by philosophical breadth of view, and on the other hand by extreme accuracy of statement. It was to the combination of these characteristics with highly skillful experimentation that the value of his research work was due. The combination is seen prefigured in his reports of researches on various problems in the domain of tropical chemistry; it is noted as realized in his published investigations on phthalic acid derivatives; but it became most effective at the Mellon Institute, where Pratt enjoyed broad opportunities to apply, in the inquiries of the Industrial Fellowships under his supervision, his profound knowledge of organic chemistry and his familiarity with research methods. His scientific spirit, his keen critical insight, and his exhaustive control of sources of information gained and held the high respect of all and played a prominent part in establishing the success of the system in operation at the Institute. To the members of the Institute the tidings of his death came with a deep sense of loss, for, in addition to being an efficient research executive, he was a lovable man.

W. A. Hamor

LEONARD MERRITT LIDDLE

The untimely death, on February 21, of Dr. Leonard Merritt Liddle, a Senior Industrial Fellow of the Mellon Institute of Industrial Research, was an irreparable loss not only to the friends whose privilege it had been to know so scholarly and amiable a man, but to the interests of the chemical profession in general. To some, perhaps, it may seem to be extravagance to refer to the irreparability of any such loss to chemistry; for in the great work of the world we are inured to see the ranks close up as heroes fall by the way, and when we come to calculate the sum of actual accomplishment, in our gratitude over the estimable results obtained we rarely perceive the importance of those innumerable unrealized possibilities upon which, in the nature of things, we can place no just evaluation. It is inevitable that this should be so. There is, however, a viewpoint from which it may be reasonably insisted that the work which rare and original minds fall short of achieving because of brevity of life does never actually get done at all. No doubt similar work is carried out; but the performance of it is in an entirely different order of causation; and while there may be a resemblance of equivalence, the fact is evident that, from the sum of human effort, an indefinite amount of rich and fruitful life has been lost. True as this is in the case of pure science, it is still more obviously true in applied science or in industrial research. This becomes clear when we consider that the work of a keen, skillful scientific investigator is artistic, the peculiar product of endless complexities of individual characteristics—personal poise, mental tone, and method of thought.

In the case of Leonard Merritt Liddle, none except the friends who knew the treasures of his highly trained, acute mind, as revealed in intimate association and in familiar conversation, are likely to realize how great is the loss which chemistry has sustained in his death. His end was very premature indeed, and it is with a deep sense of bereavement that this occasion is taken to pay a brief word of tribute to him.

Leonard Merritt Liddle, son of Stockwell and Belle Watts Liddle, was born at Mt. Vernon, Iowa, on September 11, 1885. He received his preparatory education at Cornell College Academy and was graduated in 1902. He then entered Cornell College, from which institution he received the degree of B.S. in 1906. It was while a student at Cornell that he became interested in chemistry; and after serving as principal of the Delhi, Iowa, public school during the year 1906–7, he matriculated as a graduate student in organic chemistry in the Sheffield Scientific School of Yale University. While at "Sheff," he brilliantly pursued organic research under the direction of Prof. Henry L. Wheeler, centering his inquiries on the pyrimidines; and the following is a list of the joint papers of Wheeler and Liddle:

"Researches on Pyrimidines: Thio Derivatives of Uracil and the Preparation of Uracil in Quantity," *Am. Chem. J.*, 40 (1908), 547–558.

"Researches on Pyrimidines: Synthesis of Uracil-4-Acetic Acid" *J. Am. Chem. Soc.*, 30 (1908), 1156–1160.

"Researches on Halogen Amino Acids: Iodine Derivatives of Paratoluidine; 3,5-di-iod-*p*-Aminobenzoic Acid," *Am. Chem J.*, 42 (1909), 441–461.

Liddle's graduate minor was in physiological chemistry (under Prof. Frank R. Underhill) and he maintained a lifelong interest in biochemical subjects. During the summer of 1908 he was the expert analyst of the Referee Board "Poison Squad" stationed at New Haven, under the supervision of Dr. Russell H. Chittenden, and immediately after he received his Ph.D. in June 1909, he joined the research staff of the Connecticut Agricultural Experiment Station. He spent one productive year there with Dr. Thomas B. Osborne, in investigatory work on the constitution of the proteins, and the results of his studies were reported in the following papers:

"Notes on the Analysis of Edestin and Zein," *Am. J. Physiol.*, 26 (1912), 295–304.

"Separation and Estimation of Aspartic and Glutaminic Acids," *Am. J. Physiol.*, 26 (1912), 420–426.

In September 1910 Liddle went to Grinnell College as instructor in chemistry, and three years later he accepted an Industrial Fellowship at the Mellon Institute of Industrial Research, where he spent the remainder of his short life in conducting techno-chemical investigations on vegetable and animal oils, fats, soaps, and perfumes. His researches on the refining and hydrogenation of vegetable oils (1913–16) were conspicuously valuable from an industrial standpoint, and his later work on soaps (1917) and perfumes (1918–1920) showed consistently high research ability and also resulted in the development of several processes of commercial importance. Liddle published the following papers after becoming a member of the Mellon Institute:

"Iron Carbonyl in Water Gas," *J. Ind. Eng. Chem.*, 8 (1916), 89–90.

"Occurrence of Azelaic Acid as a Product of the Spontaneous Oxidation of Fats" (with B. H. Nicolet), *J. Ind. Eng. Chem.*, 8 (1916), 416–417.

Soon after coming to the Institute, Liddle found his place and at the time of his demise he was indisputably among the foremost—in efficiency and loyalty—of the Industrial Fellows. Constantly capable of research of high order, and always alert to give generously of his profound knowledge of his specialties, he was nevertheless keenly eager for new facts and suggestions and in readiness for the revision of his opinions; and to this unfailing freshness of spirit—a candid professional vivacity which inspired ready esteem—was joined a sagacity which, naturally great, had been strengthened by a decade most fruitful in research experience. To those members of the Institute who enjoyed his friendship even in a slight way the sense of loss has been keen, for he was a very lovable man. At the time of his death he was serving as president of the Robert Kennedy Duncan Club, the organization of the Industrial Fellows of the Institute.

It has been a bitter thing to lose a research chemist of this mold, just in the prime vigor of life, and at a time when his constantly growing investigational power seemed to be making research, ever easy and pleasant to him, generously recognitory of his devotion to it. To have known such a man is an experience one cannot forget. To have had him pass away is a real misfortune to science.

W. A. Hamor

PERSONAL NOTES

Dr. A. S. Loevenhart, professor of pharmacology and toxicology at the University of Wisconsin, was elected president of the Pharmacological Society at the annual meeting held in Cleveland recently.

On the alumni lectureship in chemistry, Oberlin College has had **Dr. W. D. Bancroft,** chairman of the division of chemistry, National Research Council, lecturing on "Colloid Chemistry," and **Mr. Marsh,** of the Hercules Powder Co., lecturing on "High Explosives."

Dr. Chase Palmer, chemist of the U. S. Geological Survey, has resigned to accept a position as chief chemist in the fuel oil department of the Southern Pacific Co, Bakersfield, California.

The Chemists' Club has devised a plan by which depreciated German marks may be disposed of at the price originally paid. Those interested should communicate with the Club secretary, J. R. M. Klotz, 120 Broadway, New York City.

Dr. A. A. Noyes has resigned as professor of theoretical chemistry and director of the research laboratory of physical chemistry at the Massachusetts Institute of Technology to undertake similar duties at the California Institute of Technology.

Mr. W. L. Savell, chemical superintendent and later general superintendent of the Metals-Chemical, Ltd., plant at Welland, Ontario, and **Mr. J. G. G. Frost,** chief chemist and later chemical superintendent of the same firm, have opened a consulting office at Cleveland, Ohio.

Mr. Neil Kershaw, formerly with Procter & Gamble Co., Ivorydale, Ohio, as a member of the chemical division, has taken a position as chemist with the American Hominy Co., of Indianapolis, Indiana.

Mr. Howard Grafton, formerly chemist at the Marietta Plant of the Lavino Furnace Co., Marietta, Pa., has accepted a position with the Trumbull Steel Co., Warren, Ohio.

Mr. George A. Rankin, who resigned from the Chemical Warfare Service last July, recently returned to the Geophysical Laboratory to undertake further researches on cements.

Capt. Ross H. Dickson, Ordnance Department, U. S. A., has been recently discharged from active service and is now with the Standard Oil Co. of New Jersey as chemical engineer in the manufacturing development department.

Mr. Oscar R. Smith has resigned as assistant chief chemist of the Standard Chemical Co., Canonsburg, Pa., and has been appointed chemist and engineer of tests for the B. R. & P. Railway Co., United States Railroad Administration, stationed at DuBois, Pennsylvania.

Dr. Phoebus A. T. Levene, of the Rockefeller Institute for Medical Research, in New York, was elected associate member of the Société Royale des Sciences Médicales et Naturelles of Brussels, on December 1, 1919.

Dr. Paul Sabatier (Toulouse) and **Dr. Pierre Paul Emile Rous** (Paris) have been elected honorary members of the British Royal Institution.

Dr. Francis E. Engelhardt, milk inspector and city chemist of the City of Syracuse, N. Y., has retired. Dr. Engelhardt came to Syracuse as chemist for the Onondaga Salt Co., and while filling this position he was appointed state chemist for the Onondaga Salt Springs reservation. He became an expert on the salt deposits of this part of the state, and as such has had his share in building up the salt industry of the country. In 1877, while still holding his position with the Salt Company, Dr. Engelhardt became chemist for the City of Syracuse.

Mr. John J. Carty, president of the American Telephone and Telegraph Co., delivered a lecture on "Science and the Industries," which is the first of a series which will be held under the auspices of the National Research Council in Washington, D. C., for the purpose of stimulating interest in broad, scientific research, and to emphasize the vital connection between so-called scientific and industrial research.

Prof. Chas. H. LaWall, of the Philadelphia Section of the American Chemical Society, has received the honorary degree of Doctor of Pharmacy from the University of Pittsburgh, Pittsburgh, Pennsylvania.

Mr. Edward G. Harris has left the National Aniline & Chemical Co., Buffalo, N. Y., and has taken a position with the Niagara Sprayer Co., Middleport, New York.

Mr. H. B. Rodeman, formerly Captain in the Ordnance Department, U. S. A., stationed in Washington, D. C., has been for a number of months head of the chemical laboratory of the Duratex Co., Newark, New Jersey.

Miss Elizabeth A. Trembath, formerly with the H. J. Heinz Co., Pittsburgh, Pa., and more recently during the war emergency with the Atlas Powder Co. at their Reynolds Plant, is now process chemist for the Roessler & Hasslacher Chemical Co., at their bleaching station, Perth Amboy, New Jersey.

Mr. E. B. Clark has left the laboratories of the Ward Baking Co., and has taken charge of the laboratories of the Omaha Flour Mills Co., Omaha, Nebraska.

Mr. H. H. Tebault, formerly in the scientific department of the Pompeian Oil Co., now has charge of the business of Mead Johnson & Co., of Evansville, Ind., on the Pacific Coast, including Hawaii.

Mr. L. M. Tanner, formerly in the Chemical Warfare Service, accepted a position as superintendent of States Metal Co., Inc., Mellenville, N. Y.

Mr. C. L. McDonough has left the employ of the American Alloy Chemical Co., as chemist, and has associated himself as chemist for the Warman Steel Castings Co., of Los Angeles, California.

Mr. Frantz F. Berg, formerly chief chemist with the Burrough Bros. Manufacturing Co., Baltimore, Md., is now in charge of the pharmaceutical division of E. R. Squibb & Sons, Brooklyn, New York.

Mr. Samuel C. Levy has severed his connections as plant inspector for the Pennsylvania State Highway, and has become research chemist for the Barrett Manufacturing Co., Shadyside, New Jersey.

Mr. R. L. Comstock has left the employ of the Brown Co., Berlin, N. H., and has entered that of the Warner Chemical Co., Carteret, N. J., as plant chemist.

Mr. J. F. Johnson, formerly chemical superintendent of the Procter & Gamble Co., Cincinnati, O., has been appointed head of the chemical division of Lever Bros. Co., Cambridge, Mass.

Mr. B. F. Twining resigned as laboratory director of the Nixon Nitration Works, New Brunswick, N. J., to accept a position with the Barrett Company, Frankford, Philadelphia, Pennsylvania.

Dr. Warren K. Lewis has been appointed head of the course of chemical engineering at the Massachusetts Institute of Technology, succeeding Dr. William H. Walker who has also resigned as chairman of the administrative committee of the Institute in order to devote his entire time to the new division of industrial coöperation and research. Prof. H. P. Talbot has been appointed chairman of the administrative committee.

Mr. Gordon MacLean, formerly superintendent of the Mantle Factory, Welsbach Co., Gloucester, N. J., has become factory superintendent for Richard Hellmann, Inc., manufacturers of pure food products, Long Island City, New York.

Dr Henry Leffmann, of the Philadelphia Section of the American Chemical Society, has been elected a member of the faculty of the Philadelphia College of Pharmacy as special lecturer on research.

Mr. Carleton W. Reade, formerly chief chemist for the Delta Chemical Co., Wells, Delta Co., Mich., is now with the Marinette and Menominee Paper Co., Marinette, Wis., as chemist.

Mr. M. Harold Smith has resigned from the department of metallurgical research at the University of Utah, Salt Lake City, Utah, and has accepted a position as smoke abatement demonstrator for the Smoke Investigation Commission of Salt Lake City, Utah.

Mr. Russell B. Stoddard, formerly in the research laboratory of the National Aniline and Chemical Co., Buffalo, N. Y., is now research chemist for the Palatine Aniline & Chemical Co., Poughkeepsie, N. Y.

Mr. Philip Drinker, formerly in the technical section of the Air Service, A. E. F., is now with the Buffalo Foundry & Machine Co., Buffalo, N. Y.

Mr. I. W. Hazard resigned as laboratory director of the Gibbs Preserving Co., Baltimore. Md., to take a similar position with the Red Wing Co., of Fredonia, New York.

Mr. Frederic J. Le Maistre has severed his connection with E. I. du Pont de Nemours & Co., Wilmington, Del., and has entered into partnership with Wallace P. Cohoe, of New York.

Dr. George D. Van Epps, formerly nonferrous and oil chemist for the Continental Motors Corp., Muskegon, Mich., is at present analytical chemist for the Citro Chemical Co., Maywood, N. J.

Mr. Harris D. Hineline resigned as research engineer with the Westinghouse Electric & Manufacturing Co., to become a member of the faculty of the Science School of the Carnegie Institute of Technology, department of chemistry, Schenley Park, Pittsburgh, Pennsylvania.

Mr. Ralph W. Bridges, formerly research chemist with the International Nickel Co., and more recently metallurgical chemist in the U. S. Navy, Bureau of Steam Engineering, accepted a position in the technical department of the Aluminum Co. of America, New Kensington, Pennsylvania.

Mr. S. L. Calechman resigned as manager of the chemical and dyestuff department of the Nemours Trading Corp., to enter business for himself, with office in New York City, under the firm name of S. L. Calechman & Company.

Mr. John P. Trickey, instructor in chemistry at Northwestern University prior to service in the Chemical Warfare Service, recently accepted the position as research chemist for the Miner Laboratories, Chicago, Illinois.

Mr. Byron A. Soule, formerly chemist at the Dye Works of E. I. du Pont de Nemours & Co., Carney's Point, N. J., is now first assistant to the director of the chemical laboratory of the University of Michigan, Ann Arbor, Michigan.

Mr. Melvin B. Danheiser closed his relations as general manager of the Park Chemical Co., Cincinnati, O., and accepted a position with the Imperial Drop Forge Co., Indianapolis Ind., as metallurgical engineer.

Dr. Frank C. Whitmore resigned his position at the University of Minnesota and is now a member of the chemistry department of Northwestern University, Evanston, Illinois.

Mr. Nathan Smith, formerly connected with the R. J. Strasenburgh Co., Rochester, N. Y., as chief chemist, is now chief chemist and superintendent of the plant of the Drug Products Co., New York City.

Mr. Simon Collier left the Boston Belting Co., Boston, Mass., where he was a rubber chemist on factory research and chemical problems, to return to the Bureau of Standards, Washington, D. C., to assume charge of the Rubber Chemical Section, Mr. S. E. Epstein having resigned because of illness at home.

Mr. Edward S. Chapin, of Boston, sailed recently for Paris to succeed Mr. H. G. Stephenson as the representative of the Textile Alliance in the matter of securing vat dyes from Germany.

Dr. R. L. Jickling has resigned as research chemist with the Newport Co., Carrollville, Wis., to enter the employ of the National Aniline & Chemical Co., Inc., New York City.

Mr. Albert E. Goldstein, formerly assistant chemist in bituminous materials with the Bureau of Standards, Washington, D. C., has accepted a position as assistant chemist with the Barber Asphalt Paving Co., Madison, Illinois.

Mr. Frank L. Wright resigned as metallographist with the New Departure Manufacturing Co., to take a position as factory metallurgist with the Atlas Ball Co., Philadelphia, Pa.

Mr. Murray J. Etkins, 21 years old, of 1352 Forty-sixth St., Brooklyn, N. Y., assistant chemist at the Picatinny Arsenal, six miles north of Dover, N. J., was killed recently while trying to board a moving train.

Mr. C. L. Wiswall, for several years connected with the Hercules Powder Co., in various capacities, especially in relation to solvent recovery work, recently accepted a position as production engineer with the Vulcan Detinning Co., Sewaren, New Jersey.

Mr. Paul Pierce recently resigned as chemist and metallurgist for Savage Arms Corp., Utica, N. Y., to go with the Nordyke-Marmon Co., of Indianapolis, Ind., as chief chemist.

Mr. Charles H. Plantz, formerly connected with the Brass Rolling Mill of J. B. Wise, Inc., Watertown, N. Y., as chief chemist, has accepted a position in the engineering department of the Edison Lamp Works of the General Electric Co., at their Harrison Plant.

Mr. H. Rossbacher has assumed the duties of chief chemist of the Chicago Paving Laboratory and will supervise the routine work of the laboratory in addition to continuing investigations on the technical utilization of bituminous materials which he has been conducting for this organization since last August.

Mr. A. R. Stevenson has severed his connections with Schaar & Co., and is now with the Deegan Supply Co., Chicago, Illinois.

Prof. Carl Raymond McCrosky, formerly instructor in qualitative analysis at Oregon Agricultural College and later at the College of the City of New York, now has charge of qualitative analysis at Syracuse University, Syracuse, N. Y.

Prof. Leon A. Congdon, who was chief chemist of the State Division of Foods and Drugs of the Kansas State Board of Health and who later served in the Sanitary Corps of the U. S. Army, has taken charge of the quantitative work at Syracuse University, Syracuse, New York.

Mr. N. Gales has resigned as chemist at the United States Naval Engineering Experiment Station, Annapolis, Md., and is at present in business with his brother in New York City where they are representing the Trico Chemical Co., Inc., of Buffalo, New York.

Prof. Charles Wilson Easley, who was, respectively, associate professor, professor, and head of the department of chemistry at the University of Maine, is at the present time professor of chemical engineering at Syracuse University, taking charge of the new department of chemical engineering.

Mr. Maximilian Toch has been appointed adjunct professor of industrial chemistry in the new course at Cooper Institute, New York City.

Mr. Chauncey D. Snow, formerly assistant director of the Bureau of Foreign and Domestic Commerce, and until recently commercial attaché representing the Department of Commerce in Paris, has been appointed manager of the Foreign Commerce Department created by the National Chamber.

Mr. Harvey R. Dunbar has resigned as chemist with the United States Bureau of Mines, Washington, D. C., to become chemist with the Stonega Coke & Coal Co., Appalachia, Virginia.

Mr. Ben E. Watkins, formerly government airplane inspector at Aviation Repair Depot Montgomery, Ala., now holds a technical position with the Aluminum Company of America, Maryville, Tennessee.

Mr. Arthur Myron Breckler, vice president and chief chemist of the Eflorose Sugar Co., Cincinnati, O., was killed in an automobile accident on January 28, 1920. Mr. Breckler was a native of Bay City, Mich., and was in his thirty-fifth year. He was a graduate of Drake University, and had also studied for one year at the University of Chicago.

Dr. Harry A. Curtis has resigned as professor at Northwestern University, Chicago, to accept a position with the International Coal Products Co., New York City

Mr. Albert Hugh Bryan, chief chemist of the firm of Arbuckle Brothers, New York City, and a member of the American Chemical Society, died on January 20, 1920, of influenza, in his forty-sixth year.

Dr. Charles J. Moore, associate professor of chemistry at Hunter College, New York City, has been granted a leave of absence for one year to undertake important research work in the government laboratories in Washington, and **Dr. Minnie A. Graham,** who has been librarian and abstractor for the research department of the General Chemical Co., New York City, has been appointed as substitute for **Dr. Moore.**

The Chemical Society of the College of the City of New York is pleased to announce the following lectures for the Spring semester of 1920 to be delivered in the Doremus Lecture Theatre: HELIUM, March 29, at 4.00 P.M. **Dr. R. B. Moore,** chief chemist, U. S. Bureau of Mines. (Lantern); ROMANCE OF LEATHER MAKING, April 13, at 4.00 P.M. **Mr. R. S. Bonsib.** (Lantern); WATER SUPPLY AND DRAINAGE IN WAR CANTONMENTS, April 21, at 4.00 P.M. **Prof. D. D. Jackson,** administrative head, department of chemical engineering, Columbia University. (Lantern); MODERN COKE AND GAS MANUFACTURE (Kopper's Process) April 29, at 4.00 P.M. **Mr. E. L. Crowe.** (Lantern and Cinema); CHEMICAL NAVAL WARFARE, May 7, at 4.00 P.M. **Prof. James Kendall,** professor of chemistry at Columbia University; FIGHTING FIRE-FIREFOAM, May 14, at 4.00 P.M. **Mr. F. A. Epps,** chief engineer, the Foamite Firefoam Co. (Experimental, cinema, and lantern.)

Mr. James Gayley, recipient of the Perkin Medal of the SOCIETY OF CHEMICAL INDUSTRY in 1913 for his work in chemical metallurgy, died at his home in New York City on February 25, 1920.

Mr. H. R. Cary has resigned his position as director of Control Laboratories with E. R. Squibb & Sons to accept the position of general manager with A. L. van Ameringen, Perfumer, of New York City.

Miss Clara Bracken McMillen, of Ft. Wayne, a junior in Indiana University, was awarded the Alpha Chi Sigma Scholarship Medal in the competitive examination for 1919.

Mr. Ralph L. Dodge received appointment as junior chemist for the War Department a short time ago and is now employed as research assistant at the Fixed Nitrogen Research Laboratory, American University, Washington, D. C.

Mr. Albert D. Brokaw, formerly associate professor of economic geology and mineralogy at the University of Chicago, has opened a New York office in coöperation with four partners, under the name of Brokaw, Dixon, Donnelly, Garner & McKee, for the practice of his profession as consulting geologist.

Mr. Harry C. Helmlinger, who was formerly with the Dye Products and Chemical Co., of Newark, as chief chemist, recently became associated with the Monsanto Chemical Works in St. Louis, where he is assisting the president.

Dr. H. S. Riederer, who was formerly engaged in work on commercial chemical development at the Experimental Laboratories of the Atlas Powder Co., is now with the United Color & Pigment Co., Newark, New Jersey.

Mr. LeRoy Weil, formerly with the General Motors Corp., research laboratory, Detroit, Mich., and for a short time with the Gillespie Motor Co., of Paterson, N. J., is at present with the Hyatt Roller Bearing Co., Harrison, N. J., in the engineering department.

Mr. A. L. Meader has resigned as chemist with the Bureau of Chemistry, Food and Drug Inspection Station, New Orleans, La., to accept the position of chemist for the Southern Tobacco Products Co., Clarksville, Tennessee.

Mr. C. Harvey Sorum is now a member of the instructing staff in the department of chemistry and chemical engineering at the Massachusetts Institute of Technology, Cambridge, Massachusetts.

Mr. M. E. Pennington, formerly chief of the food research laboratory, Bureau of Chemistry, U. S. Department of Agriculture, has become manager of the research and development division of the American Balsa Co., Inc., of New York City.

Dr. Horace C. Porter, formerly of the Bureau of Mines, and later chemical engineer with the Koppers Co., Pittsburgh, and the Chemical Service Laboratories, Inc., Philadelphia, has opened an office and laboratory in Philadelphia, Pa., for consulting work in fuel testing and research.

Mr. Holland B. Slusser has resigned as chief chemist of the Hodgman Rubber Co., Tuckahoe, N. Y., to become vice president and treasurer of the Pocono Rubber Cloth Co., Trenton, New Jersey.

Dr. E. C. Sullivan has been elected vice president of the Corning Glass Works, Corning, New York.

Mr. H. M. Williams has severed his connection with the Remington Arms U. M. C. Co., to accept a position as research engineer with the General Motors Corp., Dayton, Ohio.

Mr. Alfred Watt has left the S. S. White Dental Manufacturing Co., Price Bay, N. Y., where he was employed as chemist and assayer and has accepted a position as analytical and plant research chemist in the chlorine division of the Brown Co., Berlin, New Hampshire.

Dr. Clifford J. Rolle, formerly instructor of physical and organic chemistry at the University of Cincinnati, Cincinnati, Ohio, has become research chemist for the Van Schaack Bros. Chemical Works, Chicago, Illinois.

Mr. A. J. Walker has left the Federal Rubber Co., where he was employed in the chemical laboratory, to become chief chemist for the Archer Tire & Rubber Co., of Minneapolis, Minnesota.

Mr. Hugo H. Sommer, formerly instructor in agricultural chemistry at the University of Wisconsin, Madison, Wis., is now with the Northern California Milk Producers' Association in charge of the chemical, bacteriological, and testing department.

Dr. E. P. Wightman, formerly connected with Parke, Davis & Co., Detroit, Mich., has accepted a position as research chemist with the Eastman Kodak Co., Rochester, New York.

Mr. Richard D. Leitch, after eleven months of enforced inactivity following his discharge as 2nd Lieut. in the U. S. A., has accepted an appointment as junior explosives chemist with the Bureau of Mines Experiment Station, Pittsburgh, Pennsylvania.

Mr. H. Stirling Snell has severed his connections with E. I. du Pont de Nemours & Co., where he was located at their dye works at Carney's Point, N. J., and has taken a position as chemist for William Heap & Sons, Grand Haven, Michigan.

Mr. Merrill C. Hart, formerly senior assistant chemist for the Puget Sound Navy Yard at Bremerton, Wash., is at present research organic chemist for the pharmacology department of the University of Minnesota, Minneapolis, Minnesota.

INDUSTRIAL NOTES

The Bureau of Chemistry of the U. S. Department of Agriculture has announced that decomposition in the materials used in the manufacture of catsup and other tomato products can be detected in all cases by the Howard microscopic count method. Chemical tests are not always effective in detecting spoilage resulting from mold. The Howard method has been used by the Government for over ten years, and is used by many commercial chemists and by practical catsup manufacturers in controlling the purity of their product.

The *Scientific American* reports that an English chemist has demonstrated on a laboratory scale a process which may revolutionize the methods of rubber manufacture, if it proves as successful on a commercial scale. At present the latex must be converted into rubber within 24 hours from the time it is extracted from the tree, to prevent putrefaction, but when treated by the new process it is said that it can be kept for any time. It now takes at least a fortnight to bring raw rubber into condition for transmission to the market, but the new process reduces this time to 30 minutes.

According to *Oil, Paint & Drug Reporter*, gums, among which the most valuable are the tragacanths, are produced from small shrubs which grow all over the mountains of Mesopotamia, Southern Persia. The gums are collected by rather crude methods, and no organized trade appears to exist, due largely to the difficulties of transportation and the wild and unsettled nature of the country.

The U. S. Bureau of Chemistry is investigating the use of domestic sumac, which grows wild in the United States, as a vegetable dyeing and tanning material in place of Sicilian sumac which is now used largely by American dyers on account of its deeper color. Experiments are now being conducted to determine whether an extract of equally good color can be obtained from the domestic sumac, which brings a much lower price than the imported material.

The manufacture of synthetic nitrogen on a large scale has been commenced in Sweden under a new process invented by a Swedish engineer. The company's output is now on the market, and large quantities of ammonium sulfate are being sold.

A problem confronting the granite industry in Vermont is the utilization of the immense quantities of waste granite which have collected. A small amount is used for road construction, and the use of crushed granite for bricks is being investigated. There is a considerable potash content in Barre granite, in silicate form, but recovery on a commercial scale has not been undertaken. Pulverized granite may be used in abrasive soaps, for poultry grit, and as filler in roofing and fertilizer materials, but sufficient markets have not yet been established to consume any quantity of granite, and the Bureau of Mines would welcome suggestions regarding any phase of the problem.

The American Library Association, coöperating with the Special Libraries Association, is planning a movement to further installation of technical and special libraries in industrial and manufacturing plants and associations. The National Paint, Oil and Varnish Association, National Wholesale Druggists' Association, American Drug Manufacturers' Association, International Association of Master Painters, Lithopone Institute, American Dye Manufacturers' Association, American Dye Institute, Shellac Association, American Pharmaceutical Association, American Chemical Society, and American Petroleum Institute will also coöperate in the movement.

The American Pharmaceutical Association has available a sum amounting to about $450 to be expended after October 1, 1920, for the encouragement of research. This amount either in full or in fractions will be awarded in such manner as will in the judgment of the A. Ph. A. Research Committee produce the greatest good to American Pharmaceutical research. Investigators desiring financial aid in their work will communicate with H. V. Arny, chairman, A. Ph. A. Research Committee, 115 West 68th St., New York, N. Y., before May first, giving their record and outlining the particular line of work for which the grant is desired. The committee will make recommendations to the Association at its meeting in Washington, May 3 to 8, 1920, when the award or awards will be made.

The House has passed the Agricultural Appropriation Bill, including the item of $77,000 for investigating the chemical and physical character of road materials, and $192,000 for continuing the government kelp potash plant at Summerland, California. $80,000 worth of potash produced there has been sold, and the plant is now self-supporting.

The Fairbanks, Alaska, Station of the Bureau of Mines has recently completed two series of tests to determine the comparative steaming value of Alaska lignite and spruce wood, and the resistance of lignite to weathering when stored in piles in the open. The results showed that pound for pound, the value of spruce wood lay between two samples of lignite used, but that a cord of wood is equivalent to more than a ton of lignite. The weathering tests showed that the average loss in weight through weathering was about 6 per cent, and that the weathering after 14 months was only slightly more than after one month. In large piles, only the surface to a depth of about 5 in. would be affected.

Dyestuffs reports results of tests made for the British Admiralty with a combination of coal and petroleum fuel oils for steamship fuel. It has been found possible to combine 35 per cent of pulverized coal with 20 per cent of binder and 45 per cent of oil, thereby saving considerable cost and obtaining increased heat values per barrel.

The U. S. Bureau of Chemistry at Washington has announced that the work on photosensitizing dyes begun during the war for the Bureau of Aircraft Production has made possible the preparation in the United States of all the recognized types: pinaverdol (including Orthochrome T), cyanine, pinacyanol and dicyanine; and of a new type useful for astrophotographic work. The Color Laboratory of the Bureau will place its experience at the disposal of any manufacturer who wishes to prepare these dyes for the American market, and is now prepared to supply the dyes to users at a price fixed by the Secretary of Agriculture.

The Chartered Chemical Works has recently been incorporated in Delaware with a capital of $1,000,000 for the manufacture of chemicals.

The American Clearing Co. is planning the erection of a turpentine plant at Green Cove Springs, Florida, for the extraction of pine oil, turpentine, and rosin from light wood and stumps.

According to *Commercial Fertilizer*, the recent discovery of large deposits of nitrates and potash in the Poison Hills of Prieska, South Africa, will prevent the necessity of depending on the deposits in Germany and in Chile which have heretofore had almost a monopoly. It is believed that this discovery will prove the most powerful factor in the economic reconstruction of South Africa.

The Bureau of Mines reports the discovery of an extensive asbestos claim in Arizona. The deposit is on an Indian Reservation, and under the present law development work cannot be undertaken. The American Consul at Chungking, China, reports the discovery of asbestos in Yachow and the mountains around Ta-chien-lu, although mineral specialists have not yet investigated the value of the discovery. An asbestos plant in Italy has recently begun the manufacture of asbestos pipe from Portland cement and asbestos, which is said to be lighter than iron pipe, acid proof, and corrosive proof and able to bear 450 pounds pressure per square inch. The cost of manufacture is said to be one-third of the net selling price of English iron pipe. The same company has also begun the manufacture of wall tile similar in composition to the pipe.

The U. S. Bureau of Soils has recently issued a statement in regard to work actually done and in contemplation in connection with investigating within the United States the possible sources of supply of nitrates, potash, and other natural fertilizers. The experimental plans outlined include the utilization of the cyanamide as a fertilizer, converting the war munitions plants to fertilizer factories.

In view of the almost inexhaustible supplies of earth pigments, ochers, and oxides, the manufacture of paints in South Africa promises to develop into an industry of considerable importance. Formerly all the ingredients were imported, and the local output is still far from sufficient to meet demands.

The Bureau of Mines has published a comprehensive mining glossary, covering both technical and local usage in various branches of the mining industry, as well as over two thousand Latin-American mining terms and many obsolete terms which are frequently met in research work. The glossary (Bulletin 95 of the Bureau of Mines) may be obtained from the Superintendent of Documents, Government Printing Office, Washington, D. C., at a cost of seventy-five cents.

The American Forestry Association, after a long investigation, has announced the phenomenon of sugar growing on fir trees in the Province of British Columbia. This sugar is extremely sweet and is valued at $66 a pound.

According to *Oil, Paint & Drug Reporter*, Sweden has imported dyes heavily since the signing of the armistice, chiefly from England. America has also a dye market in Sweden. The German market is apparently closed as a source of supply although before the war it was the source of practically the total supply. During the war Sweden succeeded in producing some satisfactory dyes, but at almost prohibitive prices.

The British sugar shortage, according to the *Journal of the Society of Chemical Industry*, has led to the proposal to form a company capitalized at £1,000,000 for the manufacture in England of sugar from sugar beets. A large factory is to be built, and it is hoped that the enterprise will be sufficiently remunerative to encourage the growing of sugar beets on a large scale, making the country more self-supporting in regard to the sugar supply, and also benefiting agriculture. Before the war more than 90 per cent of England's sugar supply was imported from foreign countries.

Arthur D. Little, Inc., Cambridge, Mass., is issuing a Biographic Series of pamphlets, the first three numbers of which have been printed and distributed. The subjects covered in these numbers are "Chemical Warfare," "The Production of Alcohol from Sulfite Waste Liquors," and "Industrial Research." Further pamphlets in course of preparation are: "The Automobile and Tractor at the Front," "The Electric Furnace," "Industrial Laboratories," "Molasses," "The Chemical Action of Light," "Woods and Fibers used as Paper Making Materials."

According to the *Journal of Commerce*, 47 companies were organized in January 1920 for the manufacture of chemicals, drugs, and dyes, an increase of 32 over December 1919. The total capitalization was $17,943,000 as compared with $20,145,000 for December. Nine companies were capitalized at $1,000,000 or more.

The U. S. Department of Internal Revenue has recently announced that by securing a permit, chemical and physical laboratories may use a special denatured alcohol tax-free. This denatured alcohol is made up as follows: To each 100 gal. of 95 per cent grain alcohol are added 10 gal. of pure wood alcohol of specific gravity of not more than 0.810 at 60° F.

Damage of considerably over $100,000 was caused by a fire which broke out recently at the Works Laboratory of Toch Brothers at Long Island City, N. Y., destroying the Dry Color and Chemical Works, together with several tons of fine chemicals which cannot be replaced at this time. This is the first extensive fire which Toch Brothers have had in seventy-two years.

The Tariff Commission has recently made a report to the Senate Finance Committee on the cost of manufacturing dyes in this country, embodying the results of a special investigation of the costs of thirty typical coal-tar products in 1918 and 1919. The report shows that the cost of producing these dyes in this country is from two to five times greater than the German selling prices before the war, but that they are lower than the prices at which the reparation dyes were offered, figuring the mark at par.

At the annual meeting of the stockholders of National Aniline & Chemical Co., Inc., held Feb. 16, 1920, the following directors were elected: Orlando F. Weber, H. H. S. Handy, W. N. McIlravy, W. G. Beckers, L. C. Jones, C. S. Lutkins, Henry Wigglesworth, W. J. Matheson, T. M. Rianhard, R. C. Taggesell, and F. M. Peters. The following officers of the company have been appointed: President, O. F. Weber; Vice Presidents, W. G. Beckers, J. W. Newlean; Acting Treasurer, W. H. West; Secretary, H. F. Atherton; Assistant Treasurers, H. S. Trott, T. S. Baines; Assistant Secretary, R. V. Mahon. A quarterly dividend of one and three-fourths per cent on preferred stock has been declared for the period ending March 31, 1920.

The Textile Alliance, Inc., announced on March 9, that 543 separate consignments of German dyestuffs have been held up at Rotterdam by the longshoremen's strike. 438 additional consignments are ready for shipment at the factories and will be forwarded as soon as strike conditions permit, or when arrangements can be made for shipment via another port.

The House bill relative to American participation in carrying out the trade-mark convention of Buenos Aires has recently been passed by the Senate, having been unanimously favored by the Patent Committees of both House and Senate. This legislation does not affect the domestic rights of anyone, but enables manufacturers to register their trade-marks in this country for the purpose of complying with legislation in foreign countries, which necessitates registration in the United States as a preliminary for such foreign registration. Under the present law, trade-mark pirates in foreign countries can register trade-marks of American manufacturers and thus levy blackmail upon them.

The National Aniline and Chemical Co., Inc., has withdrawn from the jobbing of all goods not of its manufacture, and will confine sales efforts to products of its own factories: dyestuffs, intermediates, food colors, coal-tar drugs, and related products.

Financial statements of the Semet-Solvay Co. and the By-Products Coke Corporation, of Syracuse, N. Y., which have just been issued show that neither company was able to pay the dividends declared from the net earnings during 1919 and that it was necessary to draw upon the surplus in order to pay the dividends. Strikes during 1919 caused losses of approximately $750,000 to the Semet-Solvay Co. H. H. S. Handy is president of both companies.

The report of the Bureau of Chemistry of the U. S. Department of Agriculture on the stocks of turpentine and rosin in the storage yards and in the hands of large dealers and jobbers throughout the country on February 2, 1920, shows a decided decrease since March 31, 1919, and indicates that the stocks will be even smaller on March 31, 1920. Stocks of some concerns manufacturing paint and varnish have not been included, but will be included in a later report covering stocks in the hands of consumers. The following table shows a comparison of stocks on hand:

	March 31, 1919	February 2, 1920
Turpentine, casks	131,288	50,926
Rosin, barrels	430,724	262,289

The Bureau of Mines of the Department of the Interior has made a thorough investigation of the effect of the removal of gasoline on the value of natural gas, and has reached the conclusion not only that the gas is not impoverished, but that removal of the gasoline is an actual benefit to the consumer. A gallon of gasoline burned in gas is worth about $1^{3}/_{4}$ cents while to the automobile owner it is worth about 30 cents, and from this source several hundred million gallons of gasoline are secured yearly which is more valuable than straight-run gasoline on account of its low boiling point. When gasoline is not removed, it causes great difficulty by condensation in the pipe lines, which results in large leakages and consequent lowering of pressure. Installation of gasoline plants eliminates most line trouble and gives better service to the public.

Representatives of the chemical and engineering societies and industries at a hearing before the House Committee on Rules on February 24, 1920, urged prompt consideration of the Nolan Bill for reorganization of the Patent Office. They stated that the Patent Office is demoralized on account of the low salaries paid, and that inventors and scientists are seriously discommoded by long delay in action and by action without proper knowledge. Without the efficient coöperation of the Patent Office which would be insured by the Nolan Bill, the American dye and chemical industries will be helpless in the face of French and German competition, according to the representative of the Manufacturing Chemists' Association, inasmuch as delay in action on American patents would admit foreign chemicals without restriction for a six months' period, probably giving them a continuous market here. The Nolan Bill has since passed the House and is awaiting action by the Senate.

At the invitation of the Federal Trade Commission, about 200 manufacturers and dealers in nitrated cellulose, pyroxylin, plastics, fibriloid, viscoloid, xylonite, etc., and also manufacturers and dealers in pyroxylin plastic products from all parts of the country participated in a trade practice submittal in Washington on March 8, 1920. This conference was for the purpose of defining practices which are considered unfair and of assisting in the elimination of methods which those engaged in the business themselves recognize as unfair, and did not mean the squashing of the separate proceedings now on the commissioner's docket.

Arrangements have been made by the Shipping Board whereby sufficient tonnage will be furnished to take care of the importation of Chilean nitrate needed as fertilizer for next season's crops. Approximately 270,000 tons will be brought to this country before July 1, and some of the shipments have already started.

After considerable discussion between importers and refiners, brokers, and others, the New York Produce Exchange has adopted regulations regarding soy-bean oil as the basis of trading by the Exchange.

The House of Representatives has set the appropriation for the next fiscal year of the Bureau of Foreign and Domestic Commerce at the same figure as last year. This is a substantial increase in the amount recommended by the House Committee on Appropriations, but is considerably less than the amount estimated by the Department as necessary for the proper carrying on of its work.

GOVERNMENT PUBLICATIONS

By Nellie A. Parkinson, Bureau of Chemistry, Washington, D. C.

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

CONGRESSIONAL COMMITTEES

Dyes and Dyeing. Public Resolution 21. 1 p. Approved November 19, 1919. To continue control of imports of dyes and coal-tar products.

Weights and Measures. House Report 477. 1 p. December 4, 1919. In re House Resolution 408, to accompany House Resolution 408, providing for consideration of House Resolution 9755, to establish standards of weights and measures for the following wheat-mill and corn-mill products, namely, flours, hominy, grits, and meals, and all commercial feedingstuffs, submitted by Mr. Campbell.

Zinc Ore. 37 pp. November 17, 1919. Hearings before subcommittee on House Resolution 6238, to provide tariff and obtain revenue in connection with metal contents of zinc ore.

Glass. 71 pp. December 12 and 13, 1919. Hearings before subcommittee on House Resolution 7785, to provide revenue for Government, to establish and maintain in the United States the manufacture of laboratory glassware, laboratory porcelain ware, optical glass, and scientific and surgical instruments.

Magnesite. Part 2. 146 pp. January 13, 1920. Hearings before subcommittee on House Resolution 5218.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

Power Characteristics of Fuels for Aircraft Engines. Report 47. 35 pp. 1920. (From Fourth Annual Report.)

(1) **Power Characteristics of Aviation Gasoline.** H. C. Dickinson, W. S. James, E. W. Roberts, V. R. Gage and D. R. Harper, 3d.

(2) **Power Characteristics of Sumatra and Borneo Gasolines.** E. W. Roberts.

(3) **Power Characteristics of 20 Per cent Benzol Mixture.** E. W. Roberts.

The following are from the Fifth Annual Report:

Glues Used in Airplane Parts with Lists of References. Compiled by S. W. Allen and T. R. Truax. Report 66. 28 pp. 1920. Prepared by Forest Service in coöperation with University of Wisconsin.

Effect of Kiln Drying on Strength of Airplane Woods. T. R. C. Wilson. Report 68. 69 pp. 1920. Prepared by Forest Service in Coöperation with the University of Wisconsin.

TARIFF COMMISSION

The Acids of Paragraph 1 and Related Materials Provided for in the Tariff Act of 1913. Tariff Information Series No. 13. 85 pp.

The report is divided into eight parts:

Part 1—*Summary*, in which are cited the portions of the tariff act of 1913 covering the commodities considered in the report, together with a brief summary of the salient facts presented in the more detailed discussion of the individual industries.

Part 2—*The boric acid and borax industry* has been investigated and detailed information pertinent to the tariff is presented. This includes the uses to which the products are put, the methods and process of manufacture, statistics for domestic production, imports and exports, and available information on domestic competition and international trade.

Part 3—*The citric acid industry* is discussed in a similar manner and special reference made to the foreign and domestic sources of the raw material and the tariff problem involved.

Part 4—*The formic acid industry* has been given like treatment and attention directed to its peculiar tariff problem.

Part 5—*The gallic, pyrogallic, and tannic acids industry* includes the manufacture of three of the acids which are closely related in their raw material and methods of manufacture.

Part 6—*The lactic acid industry* has been given similar treatment with particular reference to new commercial developments and the tariff considerations involved.

Part 7—*The oxalic acid industry* is discussed and all available information in relation to the tariff has been summarized.

Part 8—*The tartaric acid and cream of tartar industry*, like the industries discussed in Parts 3 and 5, depends upon imported raw materials. Detailed information bearing on this and other factors of tariff significance is presented.

SMITHSONIAN INSTITUTION

International Catalog of Scientific Literature, Year Ending June 30, 1919. 5 pp. From Report, 1919.

PUBLIC HEALTH SERVICE

Botulism from Eating Canned Ripe Olives. Chas. Armstrong, R. V. Story and Ernest Scott. Public Health Reports, **34**, 2877–2905 (December 19, 1919).

Health Hazards in the Industries of Niagara Falls, N. Y. P. M. Holmes. Public Health Reports, **35**, 1–20 (January 2, 1920). The twenty-one industrial plants covered by the report are divided into the following groups: abrasives, chemicals and gases; electrodes and carbon; metals and alloys; miscellaneous. Facts concerning hygienic conditions brought out by this survey indicate that industrial health hazards are preventable.

Treatment and Disposal of Sewage. H. B. Hommon, J. K. Hoskins, H. W. Streeter and H. H. Wagenhals. Public Health Reports, **35**, 101–31 (January 16, 1920). Brief descriptions of methods, processes, and structures used in the treatment and disposal of sewage in the United States, with bibliography.

Prevention of Stream Pollution by Dye and Intermediate Wastes. E. J. Casselman. Public Health Reports, **35**, 167–85 (January 23, 1920). Investigations were made as to properties and disposal treatment of several wastes of the dye and intermediate industries. Laboratory studies were made of the properties of toluidine waste, nitrobenzene waste, mono-ethylaniline waste, dye wastes, and lagoon liquor. Treatments that were successful on a 300-gal. scale and that were cheaper than evaporation were found for the lagoon liquor, the monoethylaniline wastes, and the lake-forming dye wastes; and a method of treating toluidine waste was indicated in laboratory experiments. Specific treatments of wastes were recommended to the Chemical Company of America, based on their proposed production schedule.

Botulism. Protective Measures and Cautions from the U. S. Bureau of Chemistry, Department of Agriculture. Public Health Reports, **35**, 327–30 (February 13, 1920).

Studies of the Treatment and Disposal of Industrial Wastes. Made under the supervision of Earle B. Phelps. (3) **The Purification of Tannery Wastes.** Harry B. Hommon. Bulletin 100. 133 pp. Issued November 1919.

Studies of Methods for the Treatment and Disposal of Sewage. Made under the supervision of Earle B. Phelps. **The Treatment of Sewage from Single Houses and Small Communities.**

L. C. FRANK AND C. P. RHYNUS. Bulletin 101. 117 pp. Issued December 1919. The report includes data obtained from operating testing stations at two tanneries. It gives the process of tanning hides and wastes at the two tanneries studied, descriptions of the testing stations, treatment of the wastes, the volume, analysis, and disposal of sludge. Construction data are also given for a plant to treat wastes from a tannery of 100 hides per day capacity, the effect of the tannery wastes studied on nearby water, the effect of untreated and purified tannery wastes on fish life and a bibliography of tannery wastes treatment.

HYGIENIC LABORATORY

Drugs. A. G. DUMEZ. Bulletin 119. 316 pp. Paper, 20 cents. November 1919. This is a digest of comments on Pharmacopeia of United States of America (8th and 9th decennial revisions), and National Formulary (3rd and 4th editions), calendar year 1916.

BUREAU OF INTERNAL REVENUE

Opium. Regulation 35 relating to importation, manufacture, production, compounding, sale, dispensing, and giving away of opium or coca leaves, their salts, derivatives, or preparations thereof, under Act of December 17, 1914, as amended by Sections 1006 and 1007 of revenue act of 1918, and under Section 1008 of the said Revenue Act of 1918. Revised November 1919. 78 pp.

GEOLOGICAL SURVEY

Copper Deposits of Ray and Miami, Arizona. F. L. RANSOME. Professional Paper 115. 192 pp. Paper, 75 cents.

Sunset-Midway Oil Field, California. Part II. Geochemical Relations of Oil, Gas, and Water. C. S. ROGERS. Professional Paper 117. 103 pp. Paper, 15 cents.

Ground Water in Lanfair Valley, California. D. G. THOMPSON. Water Supply Paper 450-B. Contributions to the hydrology of the United States. 22 pp. Issued January 15, 1920. This was prepared in coöperation with the Department of Engineering of the State of California.

Gold, Silver, Copper, Lead, and Zinc in the Eastern States in 1918. J. M. HILL. Separate from Mineral Resources of the United States, 1918, Part I. 8 pp. Issued January 26, 1920.

The total value of the output of gold, silver, copper, lead, and zinc in the eastern states was $27,517,488 in 1918, a decrease of over 26 per cent from the production in 1917. The total value is distributed among the various metals as follows: Gold, $14,352; silver, $106,585; copper, $4,411,058; lead, $366,243; zinc, $22,619,250.

As will be seen from the following table, the decrease in value is due to large decreases in the output of gold, copper, lead, and zinc, and reflects the condition of mining in the eastern states.

MINE PRODUCTION OF GOLD, SILVER, COPPER, LEAD, AND ZINC IN THE APPALACHIAN STATES, 1917–18

	1917	1918	Increase or Decrease
Ore sold or treated, short tons	2,709,201	2,355,688	—353,513
Gold	$29,227	14,352	—14,875
Silver, fine ounces	106,450	106,585	+135
Copper, pounds	18,061,068	17,858,535	—202,533
Lead, pounds	6,879,053	5,158,329	—1,720,724
Zinc, pounds	312,566,805	248,563,192	—64,003,613
TOTAL VALUE	$37,521,025	27,517,488	—10,003,537

Gold, Silver, Copper, Lead, and Zinc in Nevada in 1918. V. C. HEIKES. Separate from Mineral Resources of the United States, 1918, Part I. 48 pp. Issued January 27, 1920.

Gold, Silver, Copper, Lead, and Zinc in Montana in 1918. C. N. GERRY. Separate from Mineral Resources of the United States, 1918, Part I. 38 pp. Published February 26, 1920.

Gold, Silver, Copper, Lead, and Zinc in New Mexico and Texas in 1918. C. W. HENDERSON. Separate from Mineral Resources of the United States, 1918, Part I. 26 pp. Published February 19, 1920.

Gold, Silver, Copper, Lead, and Zinc in Arizona in 1918. V. C. HEIKES. Separate from Mineral Resources of the United States, 1918, Part I. 40 pp. Published February 20, 1920.

Gold, Silver, Copper, Lead, and Zinc in California and Oregon in 1918. C. G. YALE. Separate from Mineral Resources of the United States, 1918, Part I. 55 pp. Published February 24, 1920.

Gold, Silver, Copper, Lead, and Zinc in Idaho and Washington in 1918. C. N. GERRY. Separate from Mineral Resources of the United States 1918, Part I. 51 pp. Published February 27, 1920.

Gold, Silver, Copper, Lead, and Zinc in Colorado in 1917. C. W. HENDERSON. Separate from Mineral Resources of the United States, 1917, Part I. 57 pp. Published March 1, 1920.

World's Production of Petroleum. Unnumbered circular, dated January 22, 1920, giving the world's production of petroleum by countries for 1918 and total estimated production since 1857.

Our Mineral Supplies. H. D. MCCASKEY AND E. F. BURCHARD, Geologists in Charge. Bulletin 666. 278 pp. Paper, 20 cents. This is a composite of about 30 articles which have appeared separately and have been reviewed previously in THIS JOURNAL.

Mineral Resources of Alaska, Report on Progress of Investigations in 1917. G. C. MARTIN and others. Bulletin 692. 400 pp. Paper, 50 cents. The separate parts of this bulletin have been reviewed from time to time as they appeared.

Bibliography of the Metals of the Platinum Group. Platinum, Palladium, Iridium, Rhodium, Osmium, Ruthenium, 1748–1917. J. L. HOWE AND HOLTZ. Bulletin 694. 558 pp.

Porcupine Gold Placer District, Alaska. H. M. EAKIN. Bulletin 699. 29 pp.

Analysis of Silicate and Carbonate Rocks. W. F. HILLEBRAND. Bulletin 700. 285 pp. 1919. A revised and enlarged edition of Bulletin 422.

Deposits of Manganese Ore in Costa Rica and Panama. Papers by J. D. SEARS. Bulletin 710-C. Contributions to Economic Geology, 1919, Part I. 31 pp. Issued December 30, 1919. The manganese deposits thus far discovered in Costa Rica are all on the Nicoya Peninsula, on the Pacific Coast. They are widespread but mostly of low grade or small extent.

The ore bodies are intimate mixtures of various oxides of manganese. Some of the ore is amorphous and moderately soft, with enough pyrolusite to leave a black "smut" on the fingers; some is very hard and distinctly crystalline. The iron content is generally negligible. The silica is usually not in chemical combination with the ore but is mechanically mixed and occurs in grains and fine stringers. The manganese oxides are found mostly in pockets or troughs along the contact between the red metamorphic rocks and the light-colored sediments.

BUREAU OF THE CENSUS

Census of Manufactures, Mines and Quarries, Petroleum and Natural Gas, 1919, Instructions to Special Agents. Prepared under the supervision of E. F. HARTLEY. 80 pp. 1919.

BUREAU OF MINES

Report of Committee on Standardization of Petroleum Specifications, Fuel Administration, December 1918. Fuel Administration, Oil Division, Bulletin 2. 10 pp. Reprinted December 1919. This report concerns the standardization of oil specifications.

Report of Committee on Standardization of Petroleum Specifications, Fuel Administration, Effective November 25, 1919. Fuel Administration, Oil Division, Bulletin 3. 11 pp. Reprinted December 1919. Paper, 5 cents. This report concerns the standardization of gasoline specifications.

Removal of the Lighter Hydrocarbons from Petroleum by Continuous Distillation, with Especial Reference to Plants in California. J. M. WADSWORTH. Bulletin 162. Petroleum Technology 45. 162 pp. Paper, 50 cents. Issued October 1919. The purpose of this bulletin is to describe the methods of constructing and operating representative types of plants in California used for removing the light hydrocarbons from petroleum by continuous distillation, such plants being commonly known in the trade as topping or skimming plants. Limitations for recording data at the different plants made impossible the determination of a heat balance for each. The author confined himself to a comparison of the relative efficiencies of the distilling apparatus alone by the following method:

$$\text{Efficiency of stills and settings} = \frac{\text{Heat theoretically required}}{\text{Heat content of fuel consumed}}$$

Waste and Correct Use of Natural Gas in the Home. S. S. WYER. Technical Paper 257. 23 pp. Paper, 5 cents. Issued January 1920.

BUREAU OF STANDARDS

Recommended Specifications for Turpentine (Gum Spirits and Wood Turpentine). Circular 86. 11 pp. Paper, 5 cents. Issued February 16, 1920. Prepared and recommended by the United States Interdepartmental Committee on Paint Specification Standardization, October 27, 1919.

These specifications apply both to the turpentine which is distilled from pine oleoresins, commonly known as gum spirits or spirits of turpentine, and to turpentine commonly known as wood turpentine, which is obtained from resinous wood, whether by steam or by destructive distillation. When ordering under these specifications, the purchaser shall specify whether *(a)* gum spirits or *(b)* wood turpentine, is desired. When wood turpentine is specified, it may be stated whether steam or destructively distilled wood turpentine shall be furnished.

Turpentine shall be pure and conform to the following requirements:

APPEARANCE—Shall be clear and free from suspended matter and water.

COLOR—Shall be "standard" or better.

ODOR—Shall be characteristic of the variety of turpentine specified and, if desired, shall conform to the odor of the sample agreed upon.

	Max.	Min.
Specific gravity, 15.5/15.5° C	0.875	0.862
Refractive index at 20° C	1.478	1.468
Residue after polymerization with 38 N H_2SO_4:		
Gum spirits:		
Volume (per cent)	2.0	...
Refractive index at 20° C	...	1.500
Wood turpentine:		
Volume (per cent)	2.5	...
Refractive index at 20° C	...	1.495
Initial boiling point at 760 mm. pressure	160° C.	150° C.
Distilling below 170° C. at 760 mm. pressure (per cent)	...	90

Recommended Specifications for Zinc Oxide, Dry and Paste. Circular 87. 8 pp. Issued February 16, 1920. Prepared and recommended by the United States Interdepartmental Committee on Paint Specification Standardization, January 12, 1920. Zinc oxide may be ordered in the form of dry pigment or paste ground in linseed oil. Purchases shall be made on the basis of net weight.

The pigment may be American process zinc oxide, made direct from the ore, or French process zinc oxide, made from spelter. The contract shall state which kind is desired.

The color and color strength when specified shall be equal to samples mutually agreed upon by buyer and seller.

The pigment shall meet the following requirements:

	Max. Per cent	Min. Per cent
Coarse particles retained on Standard No. 200 screen[1]	0.0	..

[1] The No. 200 screen is the same as the screen formerly known as 200-mesh.

	American Process		French Process	
	Max. Per cent	Min. Per cent	Max. Per cent	Min. Per cent
Zinc oxide	...	98	...	99
Total sulfur	0.2	..	0.1	..
Total impurities, including moisture	2.0	..	1.0	..

The paste shall be made by thoroughly grinding the above pigment with pure raw or refined linseed oil. The paste shall not cake in the container and shall break up readily in oil to form a smooth paint of brushing consistency.

The paste shall consist of:

	Max. Per cent	Min Per cent
Pigment	86	82
Linseed oil	18	14
Coarse particles and "skins" (total residue left on No. 200 screen based on pigment)	0.5	..
Moisture and other volatile matter	0.5	..

Recommended Specifications for Leaded Zinc Oxide, Dry and Paste. Circular 88. 8 pp. Issued February 16, 1920. Prepared and recommended by the United States Interdepartmental Committee on Paint Specification Standardization, January 12, 1920. Leaded zinc oxide, frequently known as "leaded zinc," consists of zinc oxide and varying amounts of lead compounds. It may be ordered in the form of dry pigment or paste ground in linseed oil. Purchases shall be made on the basis of net weight.

The pigment may be high-leaded zinc oxide or low-leaded zinc oxide. The contract shall state which kind is desired. The color and color strength when specified shall be equal to samples mutually agreed upon by buyer and seller.

The pigment shall meet the following requirements:

	Max. Per cent	Min Per cent
Coarse particles retained on Standard No. 200 screen[1]	0.0	..

[1] The No. 200 screen is the same as the screen formerly known as 200-mesh.

	High-leaded		Low-leaded	
	Max. Per cent	Min. Per cent	Max. Per cent	Min. Per cent
Zinc oxide (ZnO)	...	60	...	93
Water soluble salts	1.0	..	1.0	..
Total impurities, including moisture	1.5	..	1.5	.

The balance to be normal or basic lead sulfate.

The paste shall be made by thoroughly grinding the above pigment with pure raw or refined linseed oil. The paste shall not cake in the container and shall break up readily in oil to form a smooth paint of brushing consistency. The paste shall consist of:

	Max. Per cent	Min. Per cent
Pigment	88.0	..
Linseed oil	..	12.0
Moisture and other volatile matter	0.5	..
Coarse particles and "skins" (total residue left on No. 200 screen based on pigment)	0.5	..

Thermal Expansion of Insulating Materials. W. H. SOUDER AND PETER HIDNERT. Scientific Paper 352. 31 pp. Paper, 10 cents. Issued December 27, 1919.

Constants of Radiation of a Uniformly Heated Inclosure. W. W. COBLENTZ. Scientific Paper 357. 7 pp. Paper, 5 cents. Issued January 16, 1920. The object of the paper is to give experimental data on atmospheric absorption as it affects the measurements of the radiation constants.

Efflux of Gases through Small Orifices. EDGAR BUCKINGHAM AND J. D. EDWARDS. Scientific Paper 359. 43 pp. Paper, 10 cents. Issued January 28, 1920. A theoretical and mathematical discussion.

Methods for Computing and Intercomparing Radiation Data. W. W. COBLENTZ. Scientific Paper 360. 8 pp. Paper, 5 cents. Issued January 31, 1920.

Distribution of Energy in the Spectrum of an Acetylene Flame. W. W. COBLENTZ. Scientific Paper 362. 13 pp. Paper, 5 cents.

Preparation and Reflective Properties of Some Alloys of Aluminum with Magnesium and with Zinc. R. G. WALTENBERG AND W. W. COBLENTZ. Scientific Paper 363. 5 pp. Paper, 5 cents. Issued February 12, 1920.

Materials and Methods Used in the Manufacture of Enameled Cast-Iron Wares. H. T. STALEY. Technologic Paper 142. 158 pp. Paper, 20 cents. Issued December 20, 1919. It is the purpose of this paper to deal with the materials and methods employed in the manufacture of enameled cast-iron ware. Methods of calculating enamel formulas and examples of the composition of enamels of various types are given. The defects in enamels, their causes, and the remedies to be employed in overcoming them are discussed from both the theoretical and practical standpoints. Manufacturing methods and equipment used in compounding the enamels, making and preparing the castings, and applying the enamels are also discussed. The treatise deals with the enameling of cast iron by the dry, or American, process.

A Study of the Deterioration of Nickel Spark-Plug Electrodes in Service. H. S. RAWDON AND A. I. KRYNITZKY. Technologic Paper 143. 16 pp. Paper, 10 cents. Issued January 22, 1920.

Properties of American Bond Clays and Their Use in Graphite Crucibles and Glass Pots. A. V. BLEININGER. Technologic Paper 144. 52 pp. Paper, 10 cents. Issued January 28, 1920.

DEPARTMENT OF AGRICULTURE

Quality and Value of Important Types of Peat Material. A. P. DACHNOWSKI. Department Bulletin 802. 40 pp. Paper, 10 cents. Issued December 29, 1919. A classification of peat based upon its botanical composition and physical and chemical characteristics that will aid in solving the problem of peat utilization.

A Chemical Study of the Ripening and Pickling of California Olives. R. W. HILTS AND R. S. HOLLINGSHEAD. Department Bulletin 803. 24 pp. Paper, 10 cents. Issued January 24, 1920.

Beet-Top Silage and Other By-Products of the Sugar Beet. J. W. JONES. Farmers' Bulletin 1095. 24 pp. Paper, 5 cents. Issued December 1919.

Report of the Chemist for the Fiscal Year 1919. 24 pp. Issued December 1919.

Articles from the Journal of Agricultural Research

Effect of Lime upon the Sodium Chloride Tolerance of Wheat Seedlings. J. A. LECLERC AND J. F. BREAZEALE. 18 (January 2, 1920), 347–56.

Cyanogenesis in Sudan Grass: A Modification of the Francis-Connell Method of Determining Hydrocyanic Acid. PAUL MENAUL AND C T. DOWELL. 18 (January 15, 1920), 447–50.

Invertase Activity of Mold Spores as Affected by Concentration and Amount of Inoculum. NICHOLAS KOPELOFF AND S. BYALL. 18 (February 16, 1920), 537–42.

COMMERCE REPORTS—JANUARY 1920

Research associations in England under the government's plan, whereby $4,866,500 are made available for industrial research, are becoming more frequent in connection with a number of the industries, and the formation of associations for refractory materials, nonferrous metals and Scottish shale oil has been sanctioned. (Pp. 1–2)

Phosphate deposits have been discovered in the eastern part of Holland and about 30 tons of 15 to 20 per cent phosphate are being produced daily. (P. 44)

The outlook for **American dyes** in Japan is said to be very good. (P. 55)

The German **aluminum factories**, many of which were installed during the war, may be doomed to failure unless measures are taken to protect the industry from foreign competition, and unless a way is found for maintaining the use of aluminum as a substitute for copper. (Pp. 73–4)

The beginning of work at the largest **sulfite pulp** factory in Finland is announced. (P. 85)

The olive oil industry in Palestine suffered a severe setback during the war from which it will take at least 50 years to recover. A description of the manufacture of olive and sesame oils is given. (Pp. 140–1)

A native millet is being used in the Camarines, Philippine Islands, as a **substitute for rice**. If it is found upon analysis to be thoroughly suitable for food it is believed that the rice problem of that province will be solved. (Pp. 163–4)

Huddersfield is now the most important center of **coal-tar color** making in Great Britain. A large trade is also done in **chemicals**, the most recent development being the production of drugs formerly obtained from Germany. (Pp. 169–70)

The entire stock and output of the Greek **emery** mines at Naxos have been turned over to the French government. (P. 189)

A shortage of **phosphates** in France is shown in the following table:

SUPERPHOSPHATES	Average Annual Consumption in Normal Years Amount Tons	 Phosphoric-Acid Content Tons	Average Annual Supply, 1915–1919 Amount Tons	 Phosphoric-Acid Content Tons
Mineral..........	1,950,000	273,000	750,000	105,000
Bone............	100,000	16,000	50,000	8,000
Bone, dissolved...	10,000	1,000	5,000	600
Slaggy lava.......	390,000	55,000	60,000	8,400
Natural..........	100,000	14,000	20,000	2,800
TOTAL.........	.....	359,000	...	124,800

A plan of partition and distribution is urged, whereby at least 80,000 tons per month shall reach France. (P. 219)

The United States has been allotted 379,635 lbs. of Taiwan **camphor** for the first three months of 1920. (P. 225)

A report of the **wood pulp industry** in Japan is available. (P. 236)

Advantages and uses of **cement fiber** as a by-product in cement plants in the United States are pointed out. (P. 283)

The production of **camphor** in Japan is being encouraged. (P. 312)

The Welsh **tin plate trade** is experiencing a period of great prosperity consequent upon the diminution of American competition, but a new tin plate competitor is gradually coming to the front in Japan. (P. 384)

The prospects of the **palm oil industry** are given, showing the average yield of nuts, source and recovery of the oil, trade in kernels, and the scope for new enterprises. (Pp. 386–8)

The **phosphate reserves** of the Island of Nauru in the Pacific are said to be sufficient to meet the demands of the world for 200 years. The quality of the phosphate is said to be of the highest grade. (P. 427)

The **rubber industry** in Brazil is considered to be in a critical condition because of the competition of oriental rubber. (P. 454)

Several plants for **refining oils** for export are being installed in China. (P. 462)

Attention is called to the growing demand for **artificial fertilizers** created by the agricultural development in China and Japan. (P. 462)

A new **dye-making process** was exhibited and explained at a recent meeting of the Inventors' Union in London. The colors are fluorescent and are derived from inorganic matter. (P. 467)

Zinc production in Belgium continues to increase slowly in spite of the scarcity and exceedingly high prices of raw materials. (P. 535)

A prospective shortage of **tin plate** in South Wales is reported, due to the serious lack of material for that industry. (P. 543)

The production of **nitrate** in Chile during November 1919 decreased almost 50 per cent as compared with that of November 1918. The exports showed even a greater decrease. (P. 559)

Extensive deposits of **magnesite** and **talc** which are reported in Manchuria have a great potential value. The magnesite is for the most part too pure to use for making bricks without the admixture of 7 to 8 per cent of iron. (P. 578)

Crude **bitumen** and **limestone** highly impregnated with bitumen occur in deposits around Hit, Mesopotamia, in almost unlimited quantities. Before these products can be put upon the market the limestone needs to be burned to make lime and the bitumen refined by boiling. The secrets of both processes are at present known only to local experts. (P. 587)

The International **metric system** is the sole legal standard of weights and measures in Mexico under the Mexican Law of Weights and Measures. (P. 588)

Swedish imports of **chemicals** and **dyestuffs** have been rather large and regular since the armistice was signed. Sweden produced some chemicals during the war with rather satisfactory results but the prices were almost prohibitive. Germany, as a source of supply, has been replaced by England and America. The American chemicals which will most readily find a market are wood rosin, rosin oil, heavy gas-tar naphtha, dead oil, crude carbolic acid, shingle-stain oil, and creosote oil. The prospect for American dyestuffs is regarded as very good. A list of the importations of chemicals in 1917 is given. (Pp. 615–6)

The situation in the **German chemical trade** is regarded as unsatisfactory because of the continued scarcity and increased prices of coal, soda, glue, spirits, and other materials. (Pp. 615–6)

The **Bohemian glass industry** has succeeded in maintaining its activity by indefatigable work and perseverance. There is a great shortage of coal and raw materials. Extreme difficulty is experienced in securing soda and potash and oftentimes even insufficiency of limestone and Saxon sand becomes threatening. (Pp. 624–5)

The importation of good **lime** to Peru, both hydrated and unslaked, would be a profitable enterprise. (P. 628)

SPECIAL SUPPLEMENTS ISSUED IN JANUARY

BRITISH INDIA—53*a* and 53*b* TUNIS—72*a* CHINA—55*a*

STATISTICS OF EXPORTS TO THE UNITED STATES

BRITISH INDIA—Sup. 53*a* and 53*b*

Hides and skins
Indigo
Paraffin wax
Bauxite, crude
Chemicals, drugs and dyes

CHINA—Sup. 55*a*

Castor oil
Hempseed oil
Peanut oil
Perilla oil
Soy-bean oil

TUNIS—Sup. 72*a*

Chemicals
Drugs
Hide cuttings and glues
Glue stock
Caraway seeds

COMMERCE REPORTS—FEBRUARY 1920

All restrictions have been removed from the exportation of **graphite** in Madagascar. (P. 646)

Argentina's trade in **chemicals** is reviewed, particular attention being paid to caustic soda, soda ash, chloride of lime, silicate of soda, sulfur, rosin, paraffin wax, white arsenic, chlorate and bichromate of potash, sulfuric acid, glacial acetic acid, pharmaceutical drugs, dyes, and colors. Prior to the war most of Argentina's heavy chemicals were imported from Europe but during and since the war the majority of them have come from the United States. With the advent of peace, the chemical market in Argentina is said to have entered upon a more stable condition. (Pp. 651–2)

The Connaught **tunnel** is to be lined with concrete, which is part of the electrification scheme to do away with smoke nuisance. It is also expected that the lining of concrete will eliminate the water seepage which has caused so much trouble and expense. (P. 653)

The Pan-American Financial Conference during its sessions in Washington in January 1920 endorsed the **metric system** in the following resolution:

> XIV. *Resolved*, That the conference recommends that the metric system of weights and measures be universally employed, and that, pending the attainment of that end, articles weighed and marked and shipping documents prepared according to the system of weights and measures now prevailing in the United States, should be accompanied with statements giving the equivalents under the metric system. (P. 661)

Large quantities of sugar that had been withdrawn from human consumption in Germany during the war were used in the **manufacture** of **glycerin** for war purposes. A description of the process of production is given. (Pp. 676–7)

Sheet-glass shortage in Canada has become very acute. (P. 684)

The legal measures and weights of Bulgaria are all based upon the **metric system.** (P. 687)

The production and sale of **salt** in Equador is monopolized by the government which enjoys a good profit therefrom. (P. 696)

Announcement is made of an agreement between Esthonia, Lithuania, and Lettland, on the one hand, and the National Metal and Chemical Bank on the other, whereby the bank takes over and disposes on a commission basis of the entire **flax** output of the countries named. The arrangement on the British side is that the National Metal and Chemical Bank goes into partnership with the local governments to aid the restoration of trade and production. It is reported that the agreement will result also in the reopening of the Provodnik **rubber** factory at Riga. (P. 709)

A deposit of mollusc marl has been discovered in Finland which is estimated to contain 125,000 tons of usable **marl.** Chemical analysis shows calcium oxides and 80 per cent carbonate of lime rendering the deposit important as fertilizer. (P. 712)

The French government intends to conduct a campaign in favor of the **utilization** of **crude oil.** A concrete oil pipe line is planned from Havre to Paris. (P. 725)

As a result of an official test with benzene as a motor fuel, it is hoped that benzene, together with alcohol, will solve the all-important problem of finding a cheap British-made **fuel** for **power.** (P. 725)

The Finnish government is reported to be contemplating the purchase from Germany of machinery for a **superphosphate** and **sulfuric acid plant.** (P. 732)

Kwantung Province in China is turning out over 5 per cent of the entire world's production of **bismuth.** (P. 738)

A revival of the Japanese trade in **isinglass** is reported. (P. 738)

An account is given of the **oil-bearing** seeds and **nuts** of Guatemala, of the castor oil exports, of the oil yield of cohune nuts, and of the difficulties in collecting nuts. (Pp. 778–9)

An **oil development** in **Argentina** is rumored. (P. 787)

Two important factors in the development of the **Algerian phosphate industry** are the improvement of railroads and the methods of extraction. (Pp. 788–9)

To encourage the introduction of home-made articles, a permanent **Scandinavian Industry Exposition** is contemplated in Copenhagen. (P. 829)

The **German Potash** Syndicate reports the total production of **actual potash** for 1919 at 946,000 short tons, of which 264,000 tons were sold abroad, the remainder meeting about 41 per cent of home requirements. A new increase in the schedule of prices of potash for domestic consumption of about 45 per cent is announced. The only present legal limitation over the syndicate's export activities provides that prices for foreign sales shall not be below the maximum domestic price. The possibility of dumping large amounts of potash in America at low prices seems rather remote, especially in view of the fact that the present production is far below normal. (Pp. 835–8)

A process for producing a **cattle food** from seaweed is announced from Denmark. The analysis shows the food to be nourishing and the cattle eat it willingly. It can be mixed with oil cakes. (P. 845)

The British Research Association for the Woolen and Worsted Industry is contemplating removing its headquarters from Leeds to Bradford where it will begin with the establishment of a chemical laboratory and a physics laboratory, followed as soon as convenient by the opening of engineering experimental workshops. (Pp. 846–7)

The increasing demand from the United States for supplies of **camphor** from South China is leading to a very marked activity on the part of all interests concerned in the trade. It is planned to eventually place the industry on a modern basis by the introduction of modern methods. (P. 859)

Magnesite is not available for export from Austria, as the production is limited owing to the shortage of coal. (P. 865)

A customs decision of Chile requires that the **formulas** of certain **pharmaceutical preparations** should specify not only the ingredients but also their respective proportions. (P. 881)

A bibliography on **petroleum** in Latin America has been prepared by the Bureau of Foreign and Domestic Commerce. (P. 905)

It is reported that Canton, China, is to manufacture white **newsprint paper** to meet the demand of local newspapers. (P. 917)

A new process of making **artificial silk** is reported in France. The product is known as silk cellulose, is claimed to possess great brilliancy, a remarkable solidity and durability, a touch similar to silk, and absolute imperviousness to water. At the same time, it is no more endangered by fire than the ordinary natural silks. The methods of determining artificial silk and the chemical reactions of various artificial silks are given. (Pp. 920–3)

There is a great demand for **copper, leather and other materials** in Austria. (P. 925)

A market for **wire cloth** used in the paper and pulp industry of Finland is reported. (P. 927)

A report on **mineral oil** as a factor in the United States trade is given, including statistics of imports and exports for the past six fiscal years. Particular emphasis is laid upon the demand for petroleum products during the past few years. (Pp. 932–7)

The necessity of conserving and restocking the timber lands of Quebec is noted. The importance of keeping the raw material for the use of the Canadian **pulp** and **paper plants** is emphasized. It was even intimated that the Provincial Government might have to limit the cut of the Quebec forests for the exclusive use of Quebec mills. (P. 943)

The **tanning** industry in Tientsin, China, is growing rapidly. (P. 966)

The development of the **rubber industry** in the Island of Hainan, China, promises to be a notable success. (P. 980)

Experiments have been undertaken with a view to utilizing the valuable deposits of **white clay** in the Ballarat District of Australia. It is believed that most of these deposits are especially suitable for conversion into white earthenware. (Pp. 1000–1)

The revival of the **Belgian plate and window-glass industry** is said to continue in spite of the shortage of industrial fuel and certain raw materials, notably sodium sulfate, and the transportation difficulties. (Pp. 1006–7)

The final official estimate of India's 1919–1920 **indigo** crop is 21 per cent below the final 1918–19 figures as to area and 15 per cent below as to yield. (P. 1013)

The International **metric** system is the sole standard of weights and measures in Switzerland. (P. 1016)

The Latvian government has passed a law introducing the **metric system,** but the old Russian system of weights and measures may be used where necessary until January 1, 1926. (P. 1017)

Since the armistice the production of **potash** in **Alsace** has increased by more than 300 per cent. The following statistics show the production of crude potash by months for the 11 months ending November 30, 1919:

	Tons		Tons
January	22,968	August	...
February	37,793	September	40,263
March	45,817	October	78,878
April	52,774	November	74,484
May	53,196		
June	52,916	TOTAL	508,138
July	49,049		

The mines now in operation in Alsace alone are capable of supplying the world's needs. The transportation crisis in France complicates the shipment of potash to the United States. (Pp. 1027–9)

The stocks of **mercury** at Idria are accumulating and the following statistics are given for the production of Tuscan and Idrian mercury:

The production of mercury (in tons) in the Monte Amiata (Grosseto-Siena) districts was as follows in the years 1915–1918: Ore—1915, 110,612; 1916, 132,524; 1917, 113,782; metal—1915, 985; 1916, 1,093; 1917, 1,071; 1918, 1,038. Total production of Tuscan and Idrian mercury (metal) in 1918 was: Monte Amiata (Grosseto-Siena) districts, 1,038 tons; Idria (estimate of the Italian Bureau of Mines), 600 tons; total, 1,638 tons. (Pp. 1040–1)

An account of the **Galician mineral oil industry** is given. The most recent survey gives the petroliferous survey as 47,000,000 tons. The raw petroleum of this district during recent years has given the following approximate results upon refining: 14.8 per cent gasoline; 15 per cent illuminating oil; 33 per cent gas oil; 15.7 per cent oil fats or lubricating oil; 5.5 per cent paraffin; and between 3 and 6 per cent coke, with a small percentage of waste product. Its calorific value is given at 10,770 cal., as compared with 5,000 to 6,000 cal. in coal of good quality. (Pp. 1042–7)

British export licenses for the **exportation** of all **coal-tar products,** excepting finished dyestuffs, but including aniline oils and salts, granted before January 1, 1920, are revoked, effective February 21, 1920, but renewal applications will be considered for special cause. (P. 1057)

There is a great need for **raw materials** in Riga among which the following may be mentioned:

NATIVE	FOREIGN	
Gypsum	Glass sand	Phosphate
Chalkstone	Porcelain clay	Pitch
Animal fats	Chalkstone	Rosin
Bones	Dyestuffs	Oil seed
Turpentine	By-products for dyes	Pyrites
Linseed	Crude oil	Rubber goods
Paper and wood pulp	Salts	Tanning material
	Acids	Soda

(Pp. 1084–8)

The extraction of **oil** from **Kauri-gum peat** promises to become the most important industry in New Zealand. (P. 1095)

The **Polish salt deposits** are capable of much more intense exploitation and under proper development could probably become the base of several branches of the chemical industry. The salts of Galicia are composed chiefly of kainite and sylvite. (Pp. 1097–9)

SPECIAL SUPPLEMENT ISSUED IN FEBRUARY
FRENCH WEST INDIES—31a

BOOK REVIEWS

The Outlook for Research and Invention. By NEVIL M. HOPKINS. George Washington University. x + 241 pp. and 6 photogravure portraits. D. Van Nostrand Co., New York, 1919. Price, $2.00.

One of the striking characteristics of the great war was the important rôle which chemistry, and especially the chemistry of poison gases, played in it. Equally striking was "the sudden recognition of the fundamental importance of chemical research by governments, leaders of industry and the man in the street." Because of this a book which states as its purpose "to stimulate a more general interest, not so much in what has been known as Yankee invention, but in the broader and more comprehensive American research, and to add a tiny mite towards lifting its efficiency through indicating its charm, its national worth at this time, the educational requirements to those new in the field and to point out the reasons for loss in efficiency through misconception, intense duplication work and the many snares and pitfalls awaiting the unwary inventor," should be of interest to the chemist and the general reading public as well. Hopkins accomplishes his purposes by quotations from well-known scientists and by drawing upon his own broad experience both before and during the war. After discussing the spirit of research and men of research, he takes up the question of education, some seemingly impossible problems which have been successfully solved, and then discusses industrial research in the factory. The closing chapter relates to the making and protecting of inventions. That the book is written from the viewpoint of a physicist and engineer is seen in the appendix, which lists "problems awaiting solution." According to this list, the following chemical problems await solution: chemical data for the engineering solution of problems, synthetic diamonds and foods, catalysts and the fixation of nitrogen. It would seem that there are many other industrial chemical problems that might well have been included, for the uninitiated may easily have the idea upon glancing through this list that chemistry is practically a closed art.

Perhaps the lesson we need most to learn to-day is found in the chapter on "Research in the Factory." By the use of such examples as the development of nitrocellulose and smokeless powder, the adding machine, and the high tension electrical magneto, Hopkins points out the relation of the investigator in pure science to industrial research. "While it is extremely interesting and upbuilding to think in terms of atoms and molecules, it is equally important to think in terms of large quantities of the chemical compounds that enter into reactions." This research may be carried out in one of three ways. The most expensive, but not the most costly, is the equipment of factories with modern research laboratories and the employment of able specialists. While this method can be used only by large companies, such as the General Electric Company, there are few instances where such laboratories have failed to become self-supporting and to add very materially to the quality and quantity of factory production. And when such laboratories are not abundantly self-supporting, they fail of their purpose. A second method is that proposed by the late Professor Duncan, involving the use of industrial fellowships at universities. The plan has been installed at the Universities of Kansas and Pittsburgh, and has proven satisfactory in many cases. There is only one danger attending this scheme; the university atmosphere pervades it, and the manufacturer who is willing to spend a certain sum of money, but who desires results quickly, often finds the work dragging over a long period of time. The third method, and probably the one most suited to the majority of manufacturing concerns, is to utilize the commercial laboratories which are scattered throughout the country. These are equipped with men and apparatus capable of solving practically all the industrial problems submitted to them. Since it is their livelihood, they aim to secure results as quickly as is consistent with an adequate solution of the problem, and while the finer scientific points of the investigation must of necessity be left unsolved or turned over to university men who have time for such work, the manufacturer secures information which enables him to install or correct his process and to maintain his production at a desired standard, both of quality and of quantity.

The only disappointing chapter is the one on American War Research. There we looked for some of the problems and achievements of our Chemical Warfare Service and the other scientific organizations which contributed so materially to the success of our army abroad. All we find, however, is the organization of the National Academy of Sciences and the National Research Council.

The book will prove interesting reading to those who desire to know more of that fascinating subject "research," especially as related to physics and engineering.

CLARENCE J. WEST

Colloids in Biology and Medicine. By H. BECHHOLD. Translated by J. G. M. BULLOWA. xiv + 464 pp. D. Van Nostrand Co., New York, 1919. Price, $5.00.

In view of the rapidly increasing recognition of the importance of colloid chemistry, a translation of Bechhold's book is a thing to be thankful for. Although the book deals primarily with biology and medicine, the facts that are given is in many cases of very general application and are consequently of interest to many different readers. The relation between the reactions of gelatin and the processes of tanning is self-evident. The relation of leather to hides is very similar to that of vulcanized to raw rubber. Ore flotation depends on the stabilization of bubbles by selective adsorption. The dyeing of tissues and the dyeing of textiles involve the same general principles. The emulsions of the druggist enable us to duplicate and understand some of the reactions of protoplasm.

The author treats his subject under four main heads: introduction to the study of colloids; the biocolloids; the organism as a colloid system; toxicology and pharmacology. Under the first subdivision, the titles of the chapters are: what are colloids? surfaces; size of particles, molecular weight, osmotic pressure, conductivity; phenomena of motion; consistency of colloids; optical and electrical properties of colloids; methods of colloid research. Under biocolloids the chapters are entitled: carbohydrates; lipoids; proteins; food and condiments; enzymes; immunity reactions. Under the general heading of the organism as a colloid system, we have the special subdivisions: significance of the colloidal condition for the organism; metabolism and the distribution of material; growth, metamorphosis, and development; the cell; the movements of organisms; blood, respiration, circulation and its disturbances; absorption; the nerves.

Bechhold's views in regard to starch and iodine, page 135, are very interesting.

> On account of their great surface development, the adsorptive capacity of starches is very great. As has been said, when they swell they adsorb water, dyes, etc. A very characteristic adsorption compound is formed with iodine. Iodine is the best known reagent for starches; by it they are stained blue. It was formerly believed that iodine and starch united chemically; W. Biltz (Küster) showed that it is merely an adsorption. According to the degree of adsorption, iodine solution is blue, red, orange or yellow, inasmuch as the starch solution acts as a protective colloid (W. Harrison). There are in addition varieties of starch which give at once a brownish red or a wine-red color with iodine. Inulin and lichenin are colored yellow by iodine.

It is worth noting, page 178, that

> there is a wide-spread error that stale bread has lost water and is desiccated. This is not true; the crumbling consistency of stale bread is due to a shifting of the water within the loaf; the starch grains transfer water to the albuminous framework. J. R. Katz studied this problem and found that bread kept fresh longer at 50° to 100° as well as below —10° (best in a current of air); in other words, there is a balance of swelling in starch and gluten which corresponds to that of fresh bread. At from 0° to 25° stale bread is the stable form. Staling is a particularly reversible process; dry rolls are made fresh by heating them. This is an old expedient frequently employed. The results of Katz' research on keeping bread fresh at low temperatures deserves the attention of the trade.

Wilder D. Bancroft

Les Amandes et L'Huile de Palme. By E. Baillaud and A. Stieltjes. xxiv + 346 pp. Institut Colonial de Marseille, 5, Rue Noailles, Marseille, France, 1920.

This volume of 350 pages gives a very complete view of the palm kernel oil industry up to the breaking out of the World War. It goes largely into the conditions of the industry in England, Germany, and France, considering carefully the returns from manufacturing, the capacity of the factories, problems connected with the importation of palm kernel nuts, transportation, the difference in favor of Germany at the breaking out of the war, and the actual situation of the fat and oil industry in England and France at the present time. It also contains a chapter showing the means which should be taken to develop the industry.

The greater part of the book consists of a translation of the report of the Committee on Edible Oil Producing Nuts and Seeds presented to both houses of Parliament by command of His Majesty, June 1916. This Committee made a careful investigation of the industry as it existed in England, and the report gives the minutes of the evidence taken. This translation occupies 255 pages.

The second part of the book goes very carefully into the preparation of the fruit from which the palm oil is obtained. It contains numerous descriptions and cuts of machinery used.

The third part of the book goes very particularly into the mechanical treatment for producing palm oil at Togo and Cameroun.

Part 4 of the book consists of world statistics of fats and oils compiled in 1913. The book is recommended particularly to those interested in the production and manufacture of this special product.

David Wesson

Analysis of Babbitt. By James Brakes. 169 pp. Allen Book and Printing Co., Troy, New York, 1919. Price, $2.00.

The author states in his preface that this is a small practical book on the analysis and manufacture of Babbitts and that it includes reactions and data, as well as references to many methods of analysis and an extensive bibliography on metallurgical engineering. The data comprise, for a small volume, a remarkably extensive compilation of information on the history, properties, occurrence, metallurgy, uses, and compounds of the metallic elements used in bearing metals; namely, antimony, tin, lead, and copper. These statements are evidently taken from a wide range of sources and indicate an exhaustive search of the literature. They are, however, quoted one after another as a series of notes with nothing to indicate their relative importance. Many references are given, but in many more cases the reader is left to judge of the authenticity and value of the information. Unfortunately, there are many inaccuracies and misstatements.

Very extensive information is given on the occurrence of minute quantities of tin, lead and copper in food products. Undue importance is given to the poisonous nature of the metals and statements are quoted which appear not to have been fully authenticated.

The title of the book is, in fact, not broad enough to cover its scope, and, although there are separate analytical methods given for each of the four metals, there is no complete method for quantitative analysis of Babbitt metal described consecutively. The methods described are not those generally accepted as desirable.

The bibliography covers references to over one thousand different articles and publications, both in English and other languages, and apparently includes all that was found relating in any way to the analysis and metallurgy of these four metals. This is a valuable list of references and it includes a great many relating to the analysis of Babbitt. However, much the larger number refer to articles with little relevancy to this subject, including many on the detection of traces of metals in food products and in relation to medical diagnosis. With a bibliography of such broad scope it is difficult for one studying a special subject to find the references particularly relating to it.

The last chapter, entitled "Babbitt Metal," contains notes on manufacture, mixing and sampling of Babbitt. Two formulas are given here as No. 1 and No. 2 Babbitt, which are stated to be all that are usually necessary for ordinary work. These are not generally accepted as such.

The book contains grammatical and typographical errors, although the latter are probably no more frequent than would be expected in a first edition from a non-technical press. The arrangement and type of titles and sub-heads is poor.

W. A. Cowan

Annuario per le Industrie Chimiche e Farmaceutiche—Anno I, 1918. Compiled for the Committee on the Chemical and Pharmaceutical Industries by Professors Nasini, Villavecchia, Cappelli and Meneghini with the collaboration of Doctors Fantacchiotti and Silvestri. Published by the Minister of Industry, Commerce and Labor. vi + 555 pp. Typografia Operaia Romana Coöperativa, Via Porta Cavallegeri 7A, Rome, Italy, 1919.

Very tangible evidence of the tremendous increase in Italy's chemical production during the war period is presented by this directory of her chemical and pharmaceutical industries, which is the work of the committee organized in November 1915 to coöperate with the Minister of Industry, Commerce and Labor in the war work of the industry. Data collected from manufacturers by this committee were so obviously of commercial value that it was decided to put it into permanent form. The directory gives an alphabetical list of the manufacturers, their addresses, and the products they manufacture; a similar list of chemical and pharmaceutical products with their makers; statistics of average monthly production, and of imports and exports from 1911 to 1918.

These Italian facts and figures, set down in black and white, remind us very forcibly that the United States is not the only country which has expanded her chemical industry during the war and foretell, too, the keen competition that there will be for chemical and drug products in all of the world's markets. Italian sulfur, argols, tartaric and citric acids, vegetable oils, and citrus essences have long held their place in these markets; but to-day Italy is producing lead acetate, nitric and hydrochloric acids, caustic soda, benzene, and naphthalene (to mention but a few of the products of her war expansion) all far in excess of her domestic requirements.

This carefully arranged directory will surely be of value to the Italian chemical industry in its sales efforts, for it makes immediately available just the information of sources and of output which both the foreign and domestic buyer is continually seeking.

William Haynes

NEW PUBLICATIONS

By Clara M. Guppy, Librarian, Mellon Institute of Industrial Research, Pittsburgh

Alcohol: Its Production, Properties, Chemistry, and Industrial Applications. C. Simmonds. 574 pp. Price, 21s. Macmillan & Co., Ltd., London.

Boiler Management: Efficient Boiler Management; With Notes on the Operation of Reheating Furnaces. C. F. Wade. 8vo. 266 pp. Price, $4.50. Longmans, Green & Co., New York.

Chemical Dictionary: Inorganic Chemical Synonyms and Other Useful Chemical Data. E. R. Darling. 12mo. 100 pp. Price, $1.00. D. Van Nostrand Co., New York.

Chemical Dictionary: Popular Chemical Dictionary. C. T. Kingzett. 8vo. 374 pp. Price, 15s. Baillière, Tindall & Cox, London.

Chemistry: Elementary Practical Chemistry. Part I. General Chemistry. F. Clowes and J. B. Coleman. 7th Ed. 8vo. 241 pp. Price, 6s. J & A. Churchill, London.

Chemistry: Elementary Practical Chemistry for Medical and Other Students. J. E. Myers and J. B. Firth. 2nd Ed. Revised. 8vo. 194 pp. Price, 4s. 6d. Charles Griffin & Co., London.

Chemistry: Industrial and Manufacturing Chemistry. Part B. Organic. A Practical Treatise. G. D. Martin. 5th Ed. 8vo. 744 pp. Price, 36s. C. Lockwood & Son, London.

Chemistry: A Treatise on Qualitative Analysis. Frank Clowes and J. B. Coleman. 9th Ed. 8vo. 400 pp. Price, 12s. 6d. J. & A. Churchill, London.

Dyeing Industry: Being a Third Edition of "Dyeing in Germany and America." S. H. Higgins. 189 pp. 8s. 6d. University Press, Manchester.

Graphic Charts: How to Make and Use Graphic Charts. A. C. Haskell. 8vo. 550 pp. Price, $5.00. Codex Book Co., 19 William St., New York City.

Iron: Le Fer et Ses Dérivés. L'Acier dans la Construction Automobile. Jean Delestrade. 258 pp. Price, 14fr. 50. Dunod, Paris.

Iron Bacteria. David Ellis. 8vo. 179 pp. Price, $4.00. F. A. Stokes Co., New York.

Kinetic Theory of Gases and Liquids. R. D. Kleeman. 12mo. 272 pp. Price, $3.00. John Wiley & Sons., Inc., New York.

Lime: Right Use of Lime in Soil Improvements. Alva Agee. 12mo. 89 pp. Price, $1.25. Orange Judd Co., 315 Fourth Ave., New York.

Metals: La Taille des Metaux. F. W. Taylor. 295 pp. Price, 16fr. 50. Dunod, Paris.

Milk: Le Lait. Physiologie, Analyse, Utilisation. A. Monvoisin. 2nd Ed. Revised and Enlarged. 540 pp. Price, 20 fr. Asselin et Houzeau, Paris.

Oil and Gas Prospecting: Prospecting for Oil and Gas. L. S. Panyity. 249 pp. Price, $3.25 John Wiley & Sons, Inc., New York.

Petroleum Register; An Annual Directory and Statistical Record of the Petroleum Industry in the United States, Canada and Mexico, 1919. Price, $10.00. Oil Trade Journal, Inc., New York.

Physical Chemistry: Introduction to Physical Chemistry. James Walker. 8th Ed. 8vo 433 pp Price, 16s. Macmillan & Co., Ltd., London.

Selenium Cells. T. W. Benson 8vo. 63 pp. Price, 7s. 6d. E. & F N Spon, Ltd., London.

White-Lead. Its Use in Paint. A. H. Sabin. 12mo. 133 pp. Price, $1.25. John Wiley & Sons, Inc., New York.

RECENT JOURNAL ARTICLES

Acid Phosphate: The Manufacture and Distribution of Acid Phosphate. S. L. Carter. *The American Fertilizer*, Vol. 52 (1920), No. 4, pp. 61–66.

Aluminum: Modern Foundry for Aluminum Castings. F. L. Prentiss. *The Iron Age*, Vol. 105 (1920), No. 8, pp. 535–539.

Brannerite, A New Uranium Mineral. F. L. Hess and R. C. Wells. *Journal of the Franklin Institute*, Vol. 189 (1920), No. 2, pp. 225–238.

Butyl Alcohol: Manufacture of; A Proposed Theory for the Mechanism of the Weismann Process. T. C. Newman. *Canadian Chemical Journal*, Vol. 4 (1920), No. 3, pp. 76–77.

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Charcoal: La Crise du Charbon, Ses Causes, Ses Conséquences, Propositions pour l'Atténuer. Ch. Berthelot. *Chimie et Industrie*, Vol. 3 (1920), No. 1, pp 88–96.

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Colloid Chemistry in Textile Industries. Part I. W. Harrison. *Color Trade Journal*, Vol. 6 (1920), No. 2, pp. 50–55.

Cyanide: A New Cyanide. Description of the Process for Converting Calcium Cyanamide to a New Cyanide in a Modern Sodium Chloride Solution. W S. Landis. *Chemical and Metallurgical Engineering*, Vol. 22 (1920), No. 6, pp. 265–268.

Dyeing of Human Hair. E. C. Gray. *Color Trade Journal*, Vol. 6 (1920), No. 2, pp. 63–65.

Dyestuffs: Colorimetric Evaluation of Dyestuffs. H. B. Gordon. *Color Trade Journal*, Vol. 6 (1920), No. 2, pp. 61–63.

Dyestuffs: Developing the Chinese Dyestuff Business. L. W. Alwyn-Schmidt. *Color Trade Journal*, Vol 6 (1920), No. 2, pp. 35–38.

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Glass: Glass Industry of North America. W. E. S. Turner. *Journal of the Society of Glass Technology*, Vol. 3 (1919), No. 11, pp. 166–200.

Glass Furnaces: Some Recent Improvements in the Designs of Glass-works Furnaces and Gas Producers. J. S. Atkinson. *Journal of the Society of Glass Technology*, Vol. 3 (1919), No. 11, pp. 148–166.

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Magnesite: Canadian Magnesite Industry; Notes on the Development of the Magnesite Industry in the Dominion, with Review of the Operations of Leading Companies. W. C. Phalen. *Canadian Chemical Journal*, Vol. 4 (1920), No 1, pp. 11–12.

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Sulfate Recovery: Explosion Process of Sulfate Recovery. H. K. Moore. *The Chemical Engineer*, Vol. 28 (1920), No. 1, pp 8–16.

Water-Softening: A Study of the Lime-Soda Ash Water-Softening Process. M. R. Hebrle and F. M. Gleeson. *Chemical and Metallurgical Engineering*, Vol. 22 (1920), No. 6, pp. 269–272.

MARKET REPORT—MARCH, 1920

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

		Mar. 1	Mar. 15
Acid, Boric, cryst., bbls.	lb.	.16	.17
Hydrochloric, com'l, 22°	lb.	.02	.02
Hydriodic	oz.	.19	.19
Nitric, 42°	lb.	.08½	.08½
Phosphoric, 50% tech.	lb.	.25	.25
Sulfuric, C. P.	lb.	.08	.08
Chamber, 66°	ton	22.00	22.00
Oleum	ton	27.00	27.00
Alum, ammonia, lump	lb.	.04	.04
Aluminum Sulfate (iron-free)	lb.	.03	.03
Ammonium Carbonate, pwd.	lb.	.13	.13
Ammonium Chloride, gran.	lb.	.15	.15
Ammonia Water, carboys, 26°	lb.	.10	.10
Arsenic, white	lb.	.12½	.13
Barium Chloride	ton	160.00	175.00
Nitrate	lb.	.11	.11
Barytes, white	ton	25.00	25.00
Bleaching Powd., 35%, Works,	100 lbs.	3.00	4.00
Borax, cryst., bbls.	lb.	.09	.09½
Bromine, tech., bulk	lb.	.75	.80
Calcium Chloride, fused	ton	22.00	22.00
Chalk, precipitated	lb.	.05	.05
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	8.00	8.25
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.50	1.50
Iodine, resublimed	lb.	4.10	4.10
Lead Acetate, white crystals	lb.	.14	.14
Nitrate	lb.	.15	.15
Red American	100 lbs.	.10½	.10½
White American	100 lbs.	.09½	.09½
Lime Acetate	100 lbs.	2.00	2.00
Lithium Carbonate	lb.	1.50	1.50
Magnesium Carbonate, powd.	lb.	.19	.19
Magnesite	ton	65.00	65.00
Mercury flask	75 lbs.	87.00	92.00
Phosphorus, yellow	lb.	.35	.35
Plaster of Paris	100 lbs.	1.50	1.50
Potassium Bichromate	lb.	.34	.34
Bromide	lb.	.90	.90
Carbonate, calc., 80–85%	lb.	.24	.24
Chlorate, cryst.	lb.	.15	.15
Cyanide, bulk, 98–99%	lb.	.30	.30
Hydroxide, 88–92%	lb.	.30	.30
Iodide, bulk	lb.	3.35	3.10
Nitrate	lb.	.14	.14
Permanganate, U. S. P.	lb.	.75	.80
Salt Cake	ton	17.00	18.00
Silver Nitrate	oz.	.81½	.78½
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	2.50	3.25
Caustic, 76%	100 lbs.	5.00	7.00
Sodium Acetate	lb.	.25	.25
Bicarbonate	100 lbs.	2.25	2.25
Bichromate	lb.	.22	.22
Chlorate	lb.	.12	.12
Cyanide	lb.	.27	.27
Fluoride, technical	lb.	.15	.15
Hyposulfite	100 lbs.	3.60	3.60
Nitrate, 95%	100 lbs.	3.85	3.85
Silicate, 40°	lb.	.02	.02
Sulfide	lb.	.05	.05
Bisulfite, powdered	lb.	.05	.05
Strontium Nitrate	lb.	.25	.25
Sulfur, flowers	100 lbs.	3.75	3.75
Crude	long ton	30.00	30.00
Talc, American, white	ton	20.00	20.00
Tin Bichloride	lb.	.21½	.21½
Oxide	lb.	.60	.60
Zinc Chloride, U. S. P.	lb.	.50	.50
Oxide, bbls.	lb.	.12	.12

ORGANIC CHEMICALS

		Mar. 1	Mar. 15
Acetanilid	lb.	.62	.65
Acid, Acetic, 28 p. c.	100 lbs.	3.75	3.75
Glacial	lb.	.12¾	.12¾
Acetylsalicylic	lb.	1.00	1.00
Benzoic, U. S. P., ex-toluol	lb.	.90	.90
Carbolic, cryst., U. S. P., drs.	lb.	.15	.15
50- to 110-lb. tins	lb.	.21	.21
Acid (*Concluded*)			
Citric, crystals, bbls.	lb.	1.05	1.15
Oxalic, cryst., bbls.	lb.	.43	.45
Pyrogallic, resublimed	lb.	2.50	2.50
Salicylic, bulk, U. S. P.	lb.	.55	.55
Tartaric, crystals, U. S. P.	lb.	.72	.75
Trichloracetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.14	.14
Alcohol, denatured, 190 proof	gal.	.77	.82
Ethyl, 190 proof	gal.	6.00	6.00
Wood, 95%	gal.	2.50	2.75
Amyl Acetate	gal.	4.00	4.00
Camphor	lb.	3.00	2.60
Carbon Bisulfide	lb.	.06	.07
Tetrachloride	lb.	.11	.11
Chloroform, U. S. P.	lb.	.30	.30
Creosote, U. S. P.	lb.	.75	.75
Cresol, U. S. P.	lb.	.18	.18
Dextrine, corn	lb.	.07	.06
Imported Potato	lb.	.12	.12
Ether, U. S. P., conc., 100 lbs	lb.	.19	.19
Formaldehyde	lb.	.75	.75
Glycerin, dynamite, drums	lb.	.23	.22
Starch, corn	100 lbs.	5.35	5.35
Potato, Jap.	lb.	.08	.08
Rice	lb.	.25	.25
Sago	lb.	.05	.05

OILS, WAXES, ETC.

		Mar. 1	Mar. 15
Beeswax, pure, white	lb.	.70	.70
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	.18	.18
Ceresin, yellow	lb.	.14	.14
Corn Oil, crude	lb.	.19	.19
Cottonseed Oil, crude, f. o. b. mill	lb.	.19½	.19
Menhaden Oil, crude (southern)	gal.	.95	.95
Neat's-foot Oil, 20°	gal.	2.25	2.25
Paraffin, 128–130 m. p., ref.	lb.	.11½	.11½
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs.	bbl.	17.85	18.55
Rosin Oil, first run	gal.	.97	.97
Shellac, T. N.	lb.	1.40	1.40
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.95	1.95
Stearic Acid, double-pressed	lb.	.27	.27
Tallow Oil, acidless	gal.	1.55	1.55
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	1.94	2.04

METALS

		Mar. 1	Mar. 15
Aluminum, No. 1, ingots	lb.	.32	.32
Antimony, ordinary	100 lbs.	11.75	11.75
Bismuth	lb.	2.52	2.52
Copper, electrolytic	lb.	.19	.19
Lake	lb.	.19½	.19½
Lead, N. Y.	lb.	.09¼	.09¼
Nickel, electrolytic	lb.	.45	.45
Platinum, refined, soft	oz.	155.00	155.00
Silver	oz.	1.32	1.27
Tin	lb.	.60	.60
Tungsten Wolframite	per unit	7.00	7.00
Zinc, N. Y.	100 lbs.	9.25	9.25

FERTILIZER MATERIALS

		Mar. 1	Mar. 15
Ammonium Sulfate	100 lbs.	7.50	7.25
Blood, dried, f. o. b. N. Y.	unit	8.00	8:00
Bone, 3 and 50, ground, raw	ton	48.00	48.00
Calcium Cyanamide, unit of Ammonia		4.50	4.50
Fish Scrap, domestic, dried, f. o. b. works	unit	7.25	7.25
Phosphate Rock, f. o. b. mine:			
Florida pebble, 68%	ton	Nom.	Nom.
Tennessee, 78–80%	ton	11.00	11.00
Potassium muriate, 80%	ton	230.00	230.00
Pyrites, furnace size, imported	unit	.18	.18
Tankage, high-grade, f. o. b. Chicago	unit	8.00	7.75

COAL-TAR CHEMICALS

		Mar. 1	Mar. 15
Crudes			
Benzol, C. P.	gal.	.33	.33
Cresol, U. S. P.	lb.	.18	.18
Naphthalene, flake	lb.	.08½	.08½
Phenol, drums	lb.	.15	.15
Toluol, 90%	gal.	.28	.30
Xylol, water white	gal.	.40	.40
Intermediates			
Acids:			
Anthranilic	lb.	4.00	3.00
Benzoic	lb.	.85	.85
Broenner's	lb.	1.75	1.75
Cleves	lb.	2.00	2.00
Cresylic, 97–99%	gal.	1.00	1.00
F.	lb.	3.00	3.00
Gamma	lb.	2.50	2.50
H	lb.	1.70	1.85
Metanilic	lb.	1.70	1.70
Monosulfonic F	lb.	3.00	3.00
Napthionic, crude	lb.	.70	.70
Neville & Winther's	lb.	1.90	1.90
Phthalic	lb	.60	.60
Picric	lb.	.25	.25
Sulfanilic	lb.	.35	.35
Tobias'	lb.	2.25	2.25
Amido Azo Benzol	lb.	1.15	1.15
Aniline Oil	lb.	.35	.35
For Red	lb.	.65	.65
Aniline Salt	lb.	.44	.46
Anthracene, 80–85%	lb.	.75	.75
Anthraquinone	lb.	4.50	4.50
Benzaldehyde, tech.	lb.	.75	.75
U. S. P.	lb.	1.25	1.10
Benzidine Base	lb.	1.40	1.50
Benzidine Sulfate	lb.	1.10	1.10
Diamidophenol	lb.	6.00	6.00
Dianisidine	lb.	10.00	10.00
p-Dichlorbenzol	lb.	.10	.10
Diethylaniline	lb.	1.40	1.40
Dimethylaniline	lb.	1.30	2.00
Dinitrobenzol	lb.	.33	.36
Dinitrotoluol	lb.	.40	.43
Diphenylamine	lb.	.75	.85
G Salt	lb.	.75	.80
Hydroquinone	lb.	2.00	2.00
Metol	lb.	11.50	11.50
Monochlorbenzol	lb.	.10	.12
Monoethylaniline	lb.	2.15	2.15
a-Naphthylamine	lb.	.45	.45
b-Naphthylamine	lb.	1.15	1.15
b-Naphthol, crude	lb.	.60	.60
m-Nitraniline	lb.	1.00	1.00
p-Nitraniline	lb.	1.35	1.40
Nitrobenzol, crude	lb.	.16	.16
Rectified (Oil Myrbane)	lb.	.18	.18
p-Nitrophenol	lb.	.80	.80
p-Nitrosodimethylaniline	lb.	1.90	1.90
o-Nitrotoluol	lb.	.20	.22
p-Nitrotoluol	lb.	1.15	1.15
m-Phenylenediamine	lb.	1.25	1.35
p-Phenylenediamine	lb.	2.50	2.50
Phthalic Anhydride	lb.	.75	.75
Primuline Base	lb.	3.00	3.00
R Salt	lb.	.75	.75
Resorcin, tech	lb.	3.75	4.00
U. S. P.	lb.	6.00	6.00
Schaeffer Salt	lb.	.65	.75
Sodium Naphthionate	lb.	1.10	1.10
Thiocarbanilid	lb.	.60	.60
Tolidine, Base	lb.	1.70	1.75
Toluidine, mixed	lb.	.44	.44
o-Toluidine	lb.	.30	.30
m-Toluylenediamine	lb.	1.35	1.35
p-Toluidine	lb.	1.75	1.75
Xylidene, crude	lb.	.50	.50

COAL-TAR COLORS

		Mar. 1	Mar. 15
Acid Colors			
Black	lb.	1.15	1.15
Blue	lb.	3.00	3.00
Acid Colors (*Continued*)			
Fuchsin	lb.	2.50	2.50
Orange III	lb.	1.00	1.00
Red	lb.	1.10	1.10
Violet 10B	lb.	6.50	6.50
Alkali Blue, domestic	lb.	4.75	4.75
Imported	lb.	8.00	8.00
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	2.00	2.00
Erythrosine	lb.	12.00	12.00
Indigotine, conc	lb.	3.00	3.00
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.50	1.50
Ponceau	lb.	1.00	1.00
Scarlet 2R	lb.	1.00	1.00
Direct Colors			
Black	lb.	.95	.95
Blue	lb.	1.10	1.10
Brown	lb.	1.55	1.55
Fast Red	lb.	3.50	3.50
Yellow	lb.	2.00	2.00
Violet, con't	lb.	2.20	2.20
Chrysophenine, domestic	lb.	2.50	2.50
Imported	lb.	3.80	3.80
Congo Red, 4B Type	lb.	1.60	1.60
Primuline, domestic	lb.	3.00	3.00
Oil Colors			
Black	lb.	.70	.70
Blue	lb.	1.65	1.65
Orange	lb.	1.40	1.40
Red III	lb.	1.65	1.65
Scarlet	lb.	1.75	1.75
Yellow	lb.	1.70	1.70
Nigrosine Oil, solution	lb.	.90	.90
Sulfur Colors			
Black	lb.	.30	.30
Blue, domestic	lb.	.80	.80
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.90	.90
Chrome Colors			
Alizarin Blue, bright	lb.	7.75	7.75
Alizarin Red, W. S. Paste	lb.	5.00	5.00
Alizarin Yellow R	lb.	1.50	1.50
Chrome Black, domestic	lb.	1.25	1.25
Imported	lb.	2.20	2.20
Chrome Blue	lb.	2.50	2.50
Chrome Green, domestic	lb.	1.50	1.50
Chrome Red	lb.	2.00	2.00
Basic Colors			
Auramine, O, domestic	lb.	3.25	3.25
Auramine, OO,	lb.	4.25	4.25
Bismarck Brown Y	lb.	.90	.90
Bismarck Brown R	lb.	1.20	1.20
Chrysoidine R	lb.	1.00	1.00
Chrysoidine Y	lb.	.90	90
Green Crystals, Brilliant	lb.	6.00	6.00
Indigo, 20 p. c. paste	lb.	.75	.75
Fuchsine Crystals, domestic	lb.	4.00	4.00
Imported	lb.	12.00	12.00
Magenta Acid, domestic	lb.	4.25	4.25
Magenta Crystals, imported	lb.	10.00	10.00
Malachite Green, crystals	lb.	4.50	4.50
Methylene Blue, tech	lb	2.25	2.25
Methyl Violet 3 B	lb	2.60	2.60
Nigrosine, spts. sol	lb	.85	.85
Water sol., blue	lb	.65	.65
Jet	lb	.90	.90
Phosphine G., domestic	lb.	7.00	7.00
Rhodamine B ex-con't	lb	35.00	35.00
Victoria Blue, base, domestic	lb	6.00	6.00
Victoria Green	lb	6.00	6.00
Victoria Red	lb	7.00	7.00
Victoria Yellow	lb	7.00	7.00

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

At Eschenbach Printing Company, Easton, Penna.

Volume 12 MAY 1, 1920 No. 5

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Subscription to non members, $6.00; single copy, 60 cents, to members, 50 cents. Foreign postage, 75 cents, Canada, Cuba and Mexico excepted.
Entered as Second class Matter December 19, 1908, at the Post Office at Easton, Pa., under the Act of March 3, 1879.
Acceptance for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized July 13, 1918.
Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Secretary, 1709 G Street, N W., Washington, D. C.

ST. LOUIS MEETING, AMERICAN CHEMICAL SOCIETY

DIVISIONS TO THE FRONT

Each General Meeting of the AMERICAN CHEMICAL SOCIETY has its distinctive note. The 59th Meeting, held at St. Louis, Mo., April 12 to 17, 1920, was no exception in this respect, for above all else there stood out the strength of the divisional and sectional meetings, with their strong programs, fine attendance, and spirited discussions following the presentation of the papers.

We interpret this as the return of the chemist to his normal surroundings and his resumption of problems interrupted by the call of war service. That service was thoroughly performed and its problems have been laid aside, but it is evident that the intense stimulation of the war period is being carried over into the days of peace, hence the rich outpouring of papers for the divisional programs.

The meeting was notably successful. The registration of 976 is an index of the general interest, for while there have been meetings more largely attended, nevertheless the present one was held at a point quite distant from the SOCIETY's center of membership, and during the week when the uncertainties of travel weighed heavily against the promptings of even the most enthusiastic of attendants of meetings. The classification of the attendance by states shows how widely representative was the meeting.

ATTENDANCE CLASSIFIED BY STATES

Arkansas	3	New Jersey	21
California	6	New York	54
Colorado	4	North Carolina	1
Connecticut	2	Ohio	80
Delaware	18	Oklahoma	10
District of Columbia	26	Pennsylvania	31
Georgia	6	Rhode Island	1
Illinois	152	South Dakota	2
Indiana	26	Tennessee	3
Iowa	17	Texas	9
Kansas	19	Utah	4
Kentucky	5	Virginia	2
Louisiana	5	Wisconsin	28
Maryland	4	Wyoming	1
Massachusetts	20	China	1
Michigan	16	Canada	4
Minnesota	9	Mexico	1
Mississippi	2	Holland	1
Missouri	372	Japan	1
Nebraska	9		
		TOTAL	976

The arrangements for the meeting were in the hands of an excellent local committee headed by Dr. Charles E. Caspari. Even the local weather bureau was induced to do its part towards making the meeting a success, and it responded nobly.

Two new sections held their inaugural meetings, the Sugar Section and the Leather Section, while the Dye Section assumed a place as a division of the SOCIETY. The christening of these youngest children of the parent organization was auspicious, and their programs gave proof of the sound judgment of those who had worked for their creation.

An interesting development was the program of the Rubber Division. A marked tendency to "open up" was noticeable, and the process proved delightful. It is believed that the fine example set by one of the chief laboratories in this respect marks the beginning of a new day for that division.

So, too, in the Dye Division the proportion of scientific papers to general discussion showed a marked increase, and gave promise of future programs which will attract the chemists of the dye laboratories.

Unusual interest attached to the joint symposium on colloids, the attendance at this meeting equaling that at the general opening meeting.

To confirm our judgment as to the marked excellence of the divisional and sectional meetings, we assumed the role of a reporter and secured from the several officers the following statements:

INDUSTRIAL AND ENGINEERING CHEMISTRY DIVISION

The attendance at the meetings of this division and the discussion brought forth by the papers presented may be taken as indicative of the intense industrial interest in the division, notably so in the case of the ideas brought forth in estimating the economic status of the chemist and the high ideas the manufacturers have for their requirements of the chemist's education, and the incentives they offer to research in pure as well as applied chemistry.

H. D. BATCHELOR, *Chairman*

....

BIOLOGICAL CHEMISTRY DIVISION

This division completed its program Wednesday by remaining in session until 6:20 P.M., in order that the members might attend the colloid symposium Thursday morning. We had a splendid attendance, standing room only being available for part of the time. The point which stands out most prominently is the fundamental studies which are being made in the field of biological chemistry. The papers presented were not merely reports of general observations, but nearly all of them went down into the deeper fields of the reasons underlying biological phenomena. The most important papers were perhaps those dealing with the vitamine question, and I feel that very important results were accomplished.

R. A. GORTNER, *Chairman*

....

SUGAR SECTION

The first meeting of the Sugar Section was attended by about 60 enthusiastic members representing various branches of the sugar industry in all sections of the country. Great interest was manifested in the papers which related to the general topics of saccharimeters, beet sugar chemical control and decolorizing carbons. The sugar chemists spoke of the great benefit of having organized as a section of the AMERICAN CHEMICAL SOCIETY. From the opinions of members present and absent it is believed that the attendance and program of the next meeting will be more than doubled.

C. A. BROWNE, *Chairman*

....

LEATHER CHEMISTRY SECTION

The first meeting of this section was gratifying in the number who attended and the quality and scope of the discussion of the papers presented. Many chemists working along allied lines were attracted to the meetings, and took active part in the discussions, showing that the field which has just been plowed and sown will undoubtedly bear the fruit of success.

LOUIS E. LEVI, *Chairman*

....

AGRICULTURAL AND FOOD CHEMISTRY DIVISION

The meeting of this division was particularly well attended and the papers presented were both interesting and important. Perhaps the most significant feature of the meeting was the earnest and intelligent discussion which each of the papers brought forth, and which was equally as valuable to the author as to the division. Of the fifteen papers on the program, twelve were actually read; the railroad conditions having prevented several members from reaching St. Louis. These conditions also prevented several papers from reaching the secretary in time to be placed on the printed program, so, according to the rules of the SOCIETY, they could not be read at this meeting. The general opinion was that the divisional meeting was in every way successful.

C. E. COATES, *Chairman*

ORGANIC CHEMISTRY DIVISION

A successful session showing the present interest in the making of organic substances, reflecting the great commercial activity in dyes, pharmaceuticals, and other organic products, was held. Organic chemistry is the field in which we have been furthest from national independence, but great strides are now being made in bringing organic research and applied organic chemistry together.

E. Emmet Reid, *Chairman*

....

RUBBER DIVISION

Less and less secrecy is being maintained by the different companies regarding their research work in the development of rubber compounding. The meetings are getting to be of increasing interest as this move gains favor. The division expressed its disapproval of the marketing of compounding ingredients and accelerators under trade names, such compounds being of a poorer grade than standard or mixed with other cheaper material. The composition of these materials will be exposed to the public. The necessity for coöperative research in the rubber industry becomes more and more apparent. The chemists are really starting to get together on this.

Arnold H. Smith, *Secretary*

....

PHYSICAL AND INORGANIC CHEMISTRY DIVISION

The papers and discussions in this division seemed to divide into three main subjects: chemical reactivity and catalysis, the structure of the atom, and colloids. New studies bearing on the quantum theory seem to indicate that it is possible to calculate the speed of reactions from measurement of energy given off from atoms. It was suggested that all chemical activity may be caused by radiation. Announcement was made of the discovery of meta-chlorine, and the indication therefrom of the existence of a whole new species of atoms. The colloid symposium, arranged jointly by several divisions, aroused so great interest that the general meeting room was filled to overflowing. The papers presented brought out the practical applications of colloidal chemistry to a variety of industries.

W. D. Harkins, *Chairman*

....

DYE SECTION

The meeting was very successful and the great interest shown fully justified the Council's action in raising the youthful section to the dignity of a division. Only three of the twenty-one papers were read by title. An account of the dye patents of the Chemical Foundation was very elucidating as to the methods by which licenses can be obtained. The use which will be made of the earnings of the Foundation in fostering chemical research was brought out. A paper on dye research also created considerable interest and discussion. Among other interesting papers was one on the physical constants of aniline, bringing out particularly its hygroscopic quality. The number and quality of the papers from the Color Laboratory of the Bureau of Chemistry of the Department of Agriculture added much to the interest of the session. The members of the section seemed filled with enthusiasm and awake to their responsibilities. Keen interest was shown in the legislative situation affecting the industry represented, and a universal hope for its early enactment. The resolutions passed by the Council were read to the division, and the technical progress made in this country was reviewed.

Chas. L. Reese, *Chairman*

....

WATER, SEWAGE AND SANITATION DIVISION

The meeting of this division was very well attended, the program was carried out in full, and the various papers evoked considerable discussion. Dr. Bartow's report of the Sewage Disposal Committee of the National Research Council contained a great deal of interesting material. It is expected that at the Chicago meeting the further report of this work will be one of the most important features of the program. Some of the tests are to be conducted in the vicinity of Chicago, and will probably be ready for inspection in September. The matter of activated sludge and other methods proposed for the treatment of the sewage, especially the effluents from industrial plants, is a matter of extreme public importance, both from the standpoint of health and the general improvement of community conditions. The paper outlining the study of sewage and trade wastes at Bridgeport, Conn., furnished an interesting basis for this latter discussion.

W. W. Skinner, *Secretary*

....

PHARMACEUTICAL CHEMISTRY DIVISION

Our meeting was well attended, the most important discussion centering around the subject of the stability, chemistry, and pharmacology of chloramine antiseptics. New work on hypnotics and anesthetics was reported. The division made important recommendations to be laid before the Society's committee on the revision of the forthcoming pharmacopeia at the decennial convention. Steps were taken toward the changing of the name of the division to that of Chemistry of Medicinal Products Division. It is felt that this is a less restricted term, and will place the accent on chemistry rather than pharmacy.

Chas. E. Caspari, *Chairman*

MATTERS OF BUSINESS

In spite of the difficulties incident to travel during the week of the railroad strike, 97 members of the Council, some more or less delayed, assembled at the University Club, President Noyes presiding. The proceedings of the lengthy session were broken by the delightful dinner served in the rooms of the Club.

Great interest attached to the many valuable reports of committees which were summarized by the President. Six of these reports are printed on pages 438 to 443 of this issue. By ballot of the Council vacancies on the Committee on National Policies (Advisory Committee) were filled. Dr. H. E. Howe will take the place of Dr. M. C. Whitaker, who was ineligible for reëlection, and Dr. George D. Rosengarten will fill the unexpired term of Dr. B. C. Hesse, resigned. This committee was enlarged by the addition of two *ex-officio* members, the editors of the *Journal of the American Chemical Society* and the *Journal of Industrial and Engineering Chemistry*. Dr. A. V. H. Mory was elected councilor-at-large to fill the vacancy caused by the election of Dr. W. A. Noyes to the presidency.

Much interest attached to the selection of the place for holding the next Spring Meeting. The invitation of the Rochester Section was accepted. An invitation from the Pittsburgh Section for the Annual Meeting of 1921 was under the constitution laid on the table. After prolonged discussion and a statement of the preference of the members of the Chicago Section it was voted that it would be inadvisable to hold the 1920 Annual Meeting during convocation week with the A. A. A. S., the Council fixing the second week in September as the time for the Annual Meeting.

Dr. Charles L. Parsons was appointed to represent the Society at the International Union of Pure and Applied Chemistry in Rome in June 1920.

A measure of international significance was the acceptance by the Society of the invitation of the American Metric, the London and Manchester Decimal Associations, and the World Trade Club to join in forming a World Metric Standardization Council, and calling a conference in San Francisco in May 1920.

Continued thefts of platinum in various laboratories gave rise to serious consideration of the question of possibly overcoming this by congressional legislation. A committee was appointed to consider carefully this question.

The question of the difficulties attendant upon the manufacture, sale, and use of stills under the Bureau of Internal Revenue regulations was brought to the attention of the Council in a forcible manner by Mr. H. J. Cary-Curr, of Chicago. A committee was appointed to confer with the officers of the Bureau and to formulate suggestions which might be acceptable to the Bureau and give the needed relief.

The following resolution was unanimously adopted by the Council and ordered telegraphed to members of the Senate Finance Committee.

> The American Chemical Society through its representative Council urges upon our Senators the necessity of prompt passage of the Longworth Bill in the form reported by the Senate Finance Committee. Under the absolute protection afforded by the blockade of German ports and encouraged by the favorable legislation of the preceding Congress the coal-tar chemical industry has grown by leaps and bounds. But to meet the unusual competition threatened from the present unified German industry far greater safeguards must be established than were formerly considered necessary. The delay in enacting such legislation has caused the withholding of large amounts of capital and the creation of an atmosphere demoralizing to research and to the technical development of the industry. We feel that the fate of this industry lies now with the United States Senate and we urge the enactment of the bill as originally reported to the Senate by its Finance Committee, convinced that this legislative support will speed the industry's complete development, thereby assuring American consuming interests freedom from outside domination and providing a powerful factor in national defense.

The question of inadequate pay of professors in the universities, of the injustice of the situation, in view of the high cost of living, and of the danger involved to the whole structure of chemical education was given serious and earnest consideration by the Council. As a result of this discussion a committee was appointed to draft resolutions to be presented to official bodies.

The full proceedings of the Council Meeting are printed in the May issue of the *Journal of the American Chemical Society*.

At a well attended session of the Directors of the SOCIETY two matters were approved which affect to a marked degree the work of the *Journal of Industrial and Engineering Chemistry*. It was voted to appoint the Chemical Catalog Company, Inc., 1 Madison Avenue (Metropolitan Tower, 17th Floor), New York City, to conduct the advertising business of the SOCIETY, under the direction of the Editor of the *Journal of Industrial and Engineering Chemistry*. This arrangement was approved as of April 1, 1920. This company has a strong staff, a wide touch with the chemical industries, and has proved its ability to make a success of its undertakings. It is felt that under this new policy the power of the Journals of the SOCIETY as advertising mediums will be largely increased.

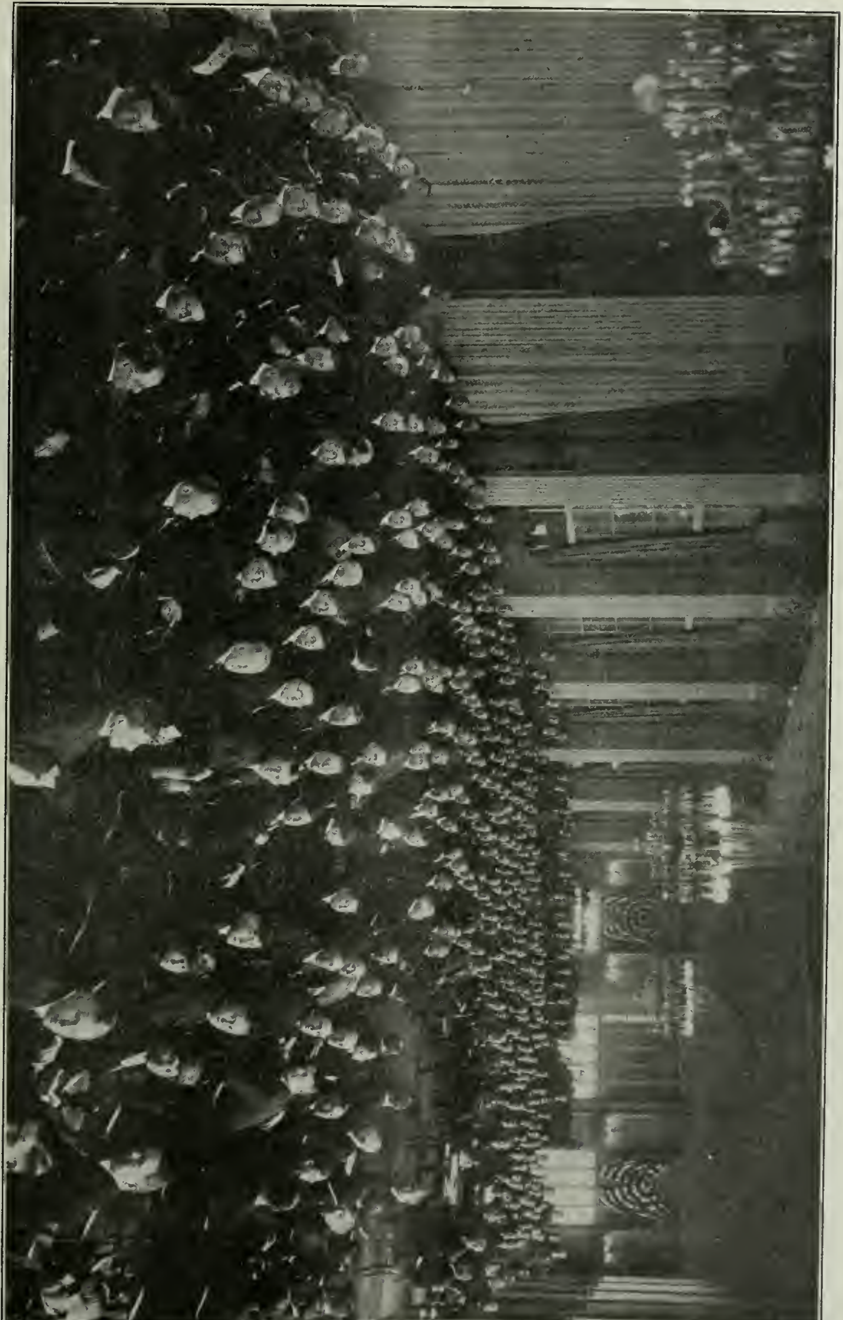
The Directors approved the leasing of space in the Metropolitan Building, 1 Madison Avenue, New York City, for the editorial headquarters of THIS JOURNAL. This change was necessitated by the exorbitant increase in rent at the old location. The move to the new quarters on the thirty-fourth floor of the tower was effected during the past week.

GENERAL MEETING

On Tuesday morning, April 13, the large ballroom of the Hotel Statler was filled with members for the opening general session. Dr. Charles E. Caspari, Chairman of the Local Executive Committee, presided, and introduced Mayor Henry W. Kiel, who extended a cordial welcome to the Society and expressed his best wishes for a successful meeting. In responding, President Noyes touched upon a vital situation in the life of our science, speaking in part as follows:

> It is with very great pleasure that we meet in St. Louis at this time. We remember the long and honorable record of your city in matters of education and the cultivation of the sciences. We remember that here you have the great Washington University and Medical School. The Missouri Botanical Gardens have made the name of St. Louis famed to the botanists of the world, and we remember many other ways in which St. Louis has fostered education and science. Not least among these, some of us remember with the greatest pleasure the meeting of the chemists in this city seventeen years ago, at the time of the Exposition, which was unique among the expositions of the world, the Congress of Arts and Sciences. In our own science there were gathered such men as Arrhenius, Ramsay, van't Hoff, Moissan, Ostwald, and Sir Ernest Rutherford, six or seven chemists whose names at that time could not be equaled with another six or seven in the whole world, and St. Louis gathered those men here in the Congress of Arts and Sciences, and many of us are very grateful for what she did at that time, so it is with pleasure that we meet in St. Louis now. On our side we are thankful for the growth of this Society, now numbering, our Secretary tells me, over 15,000 chemists, an organization that is not equaled in its character and numbers by any other scientific organization in the whole world—an organization which is nearly more than twice in number that of any other organization of chemists in the world. When our Secretary assumed office only thirteen years ago we had a budget of perhaps $30,000, I have forgotten the exact numbers, and a membership of only 3,000; now the annual budget is more than $200,000. And we are now as chemists standing almost at the parting of the ways in our science in America. Chemistry is going forward into new achievement as never before in the history of our science in this country, almost as never before in the world, and this Society of ours is the organization upon which devolves the duty of helping in this tremendous development which is upon us. Yesterday afternoon and evening some of us worked for some six or eight hours upon the business of the Society. Many important things were done: I could not this morning, if I would, adequately summarize the work of that meeting and of literally dozens of men who have been at work upon our committees and have brought to us reports of great value, merely summarized in that meeting last night. Our Society and its Council took important action in various directions. There is only one, however, that I will mention, because it is most vital to our profession at the present time. This was the action urging upon presidents, boards of trustees and all others who support educational institutions to provide adequate compensation for the teachers of chemistry in our colleges and universities. Many of us in that work know that the present time is critical in the education of chemists, and we know that that education lies at the very foundation of the development which must come in chemistry in America if we would not fail in the work that should be done, and so it is of the greatest importance that the present tendency of our best young men to go into the industries should be checked in some way or other, if we are to have a solid foundation for the future. And more than that, another item which was not emphasized so much in the Council Meeting, one of the pitiful situations in the teaching profession at the present time is the fact that so many of our young men who go into teaching are in their younger years so overloaded with a heavy burden of teaching that research and professional growth are almost impossible. That is almost more serious than the financial difficulty. If our young men have to face both lack of time for research and an inadequate salary, the future of chemical education in America is in a very sad way.

The presiding officer then turned the chair over to President Noyes, and Secretary Parsons presented the nomination by the Council of Ernest Solvay, of Belgium, for honorary membership in the Society, and a unanimous election resulted. A memorial on the death of Professor Alfred Werner, of Zurich, honorary member of the Society, was presented and adopted.



Opening Session, 59th Meeting of the American Chemical Society, Hotel Statler, St. Louis, Mo., April 13, 1920

It was announced that owing to the legislative situation in Washington, Hon. E. P. Costigan, of the Tariff Commission, had been forced to cancel his engagement to speak. At the last moment the local committee was fortunate in securing an address by Mr. Paul W. Brown, editor of *America at Work*, who spoke on "The Physical Basis for the Economic Development of the Mississippi Valley." While the subject was an unusual one for an address before the AMERICAN CHEMICAL SOCIETY, the delightful method of presentation held the close attention of the audience. Following Mr. Brown an address was made by the editor of the *Journal of Industrial and Engineering Chemistry*, which is printed on page 429 of this issue.

EDWARD MALLINCKRODT, SR., HONORARY CHAIRMAN, EXECUTIVE COMMITTEE

An interesting and suggestive development of the St. Louis meeting was an informal gathering of all chairmen and secretaries of local sections present, twenty-eight in number. It was felt that the local sections have so many problems in common that a conference of these officers at each General Meeting would bring light upon these problems from many different angles, and that from a joint exchange of experiences in the conduct of local sections valuable points could be gained for furthering this important feature of the SOCIETY'S organization. As a result of the deliberations of this gathering a recommendation was made to the Council that there be formed a section of Local Section Officers, to hold one session at each General Meeting. Pending formal action by the Council on this matter provisional officers were elected: Professor R. H. McKee, of the New York Section, Chairman, and Dr. Edgar B. Carter, of the Indianapolis Section, Secretary, to formulate plans for such a conference at the Chicago meeting.

On Wednesday evening in the auditorium of the Central High School an address on "Chemical Warfare" was given before a large and enthusiastic audience by Lt. Col. Amos A. Fries, head of the Chemical Warfare Service. Colonel Fries brought to the subject many new points of view and his narration of experiences at the Front during the war gripped his audience in deeply sympathetic interest. Colonel Fries paid glowing tribute to individual chemists who had served under him in the trying days of the formation of the Service. At the conclusion of his address graphic moving pictures of gas warfare were exhibited, which showed more clearly than words could tell the actual experiences of the men at the Front.

ENTERTAINMENTS AND EXCURSIONS

On Tuesday evening a delightful smoker was enjoyed by more than 800 chemists. On Thursday evening the banquet was held in the Hotel Statler ballroom, at which Mr. A. C. Boylston, of St. Louis, was toastmaster.

Following the dinner an address was made by Mr. W. Frank Carter, president of the St. Louis Chamber of Commerce, who spoke of St. Louis as a chemical center, pointing out that the chemical industry was second only to the automobile industry in the matter of its expansion during the last few years. Mr. Carter was followed by Chancellor Frederic A. Hall, of Washington University, who spoke of the high ideals which give dignity to the work of the scientist. President Noyes, representing the AMERICAN CHEMICAL SOCIETY, spoke in sincere appreciation of the many hospitalities shown by the sections acting as hosts, and emphasized the necessity of carrying high ideals into one's scientific work if his science is to fulfill its real mission. Brief addresses were made by L. V. Redman, Chas. L. Reese, W. D. Bancroft, R. H. McKee, and Ellwood Hendrick, epitomizing the spirit of the various occasions of a highly successful week. In conclusion Dr. Caspari paid a graceful tribute to his co-workers in the various local committees, giving credit to them for the success with which the plans for the meeting had been carried out.

T. R. BALL, CHAIRMAN, REGISTRATION AND INFORMATION COMMITTEE

The gathering afforded opportunity for the getting together of various groups of members with common interests, notably reunions of chemical alumni of some of the larger universities. The Alpha Chi Sigma chemical fraternity dinner brought out an attendance of 104 members on Wednesday evening preceding Colonel Fries' address. The members of the American Institute of Chemical Engineers, of whom some forty were present, were hospitably entertained at dinner by Dr. F. W. Frerichs at his home.

L. McMaster, Head of Chemistry Department, Washington University, St. Louis, Mo.

A not unusual but always enjoyable feature of the week's program was the excursions of Thursday afternoon and Friday, notably to the LaClede Gas Works, Monsanto Chemical Works, LaClede-Christy Clay Products Plant, the Standard Oil Refinery, at Wood River, Ill., and the Illinois Glass Company, at Alton, Ill. A delightful luncheon was served at the Mineral Springs Hotel, Alton, by courtesy of the St. Louis Section.

ADDRESSES

INTRODUCTORY ADDRESS

By W. A. Noyes

Two years ago our Army in France was dependent, among other things, on what the chemists of America could do and upon the men in France who were using the materials the chemists in America could make for them; and some of us chemists have not realized perhaps as we should how far we were dependent upon the men who knew how to use those supplies in the right way in military affairs. I know from friends who were very close to Colonel Fries in the war that the Chemical Warfare Service in France was exceedingly fortunate when he was selected as its head, and we may count ourselves fortunate here in America that he is now the head of the Chemical Warfare Service of the United States. It is our great good fortune to have with us to-night the man who was at the center of things and who did things in France. He will speak to you.

CHEMICAL WARFARE

By Amos A. Fries[1]

Lt. Col., U. S. Army, Chief of Chemical Warfare Service

The old adage that "There is nothing new under the sun" is often quoted by those who would detract from the glory of a new achievement or condone the evil deeds of those who have broken the faith. The Germans did not invent poisonous gases, nor did they invent the earliest methods used in gas attacks. Neither did the Wrights invent flying, nor the basic methods used in their first flights—but to their everlasting glory they gleaned from a thousand pages the thoughts of many men in many countries, and by applying the knowledge thus acquired made flying a reality. The Germans gleaned from many lands the possibilities of poisonous gases, together with methods of using them—and to their everlasting shame broke faith with the countries then in the war, and on April 22, 1915, launched the first really effective gas attack in the history of the world.

But whatever we may think of that first attack, chemical warfare is to-day an established fact. No modern nation dares to give it up, and ere long no modern nation will want to give it up unless indeed all war can be abolished. But that day, unfortunately, is too far distant for me to take up any of your time to-night talking about it.

I am not going to discuss the chemistry of chemical warfare. I am simply going to tell you what chemical warfare is, tell you what it did in the World War, tell you something of the great part played by the chemists in that war, and, lastly, tell you the future of chemical warfare as I see it.

In the first place, chemical warfare is a complete science in itself. No other invention since that of gunpowder has made so profound a change in warfare as gas is making or will make in the future.

To-day there are only four really distinct arms of the Service, *viz.*, the Infantry, the Artillery, Aviation, and Chemical Warfare. All other forms of warfare are a combination, more or less complete, of these. The gases, smoke, and incendiary materials that make up chemical warfare are used to a greater or lesser extent by other arms, but wherever gas is used it compels precautionary measures that are found in no other branch of the Service.

No officer, however well trained in other branches of the War Department, can handle gas until especially trained in its use. It is the most universal of weapons, and as it drifts with the very air, becomes the most difficult of all methods of warfare to avoid. No form of precaution heretofore used on land or sea is effective against it. The mask and training that go with it are totally unlike any other element of war. Thus, from the laboratory to the enemy, gas warfare is new, requiring new methods, new knowledge and new training. Depending more or less upon the wind, and being affected by the weather, by the character of the ground, and by the verdure on the ground itself, chemical warfare requires the expert to take into consideration conditions which it is not necessary to consider to an appreciable extent in any other fighting branch.

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[1] Amos Alfred Fries was born March 17, 1873, in Vernon County, Wisconsin, and moved as a boy to Missouri, thence to Oregon. After a short teaching experience he entered West Point by competitive examination, graduating seventh in his class April 26, 1898. He was commissioned Second Lieutenant in the Corps of Engineers, and appointed First Lieutenant in 1901, Captain in 1904, Major in 1912, Lieutenant Colonel in 1917.

He served with Captain John J. Pershing on an expedition into the Moro country, as Chief Engineer Officer, was Director of Military Engineering at the Engineer School, Washington Barracks, Washington, D. C., from 1911 to 1914, and at the outbreak of the war was in charge of the construction of roads and bridges in Yellowstone National Park. Perhaps his chief work with the Corps of Engineers was in connection with the improvement of Los Angeles Harbor.

Leaving Yellowstone Park July 15, 1917, he reached Paris August 14, nd was assigned as Director of Roads, but five days later was appointed Chief of the Gas Service, A. E. F., which position he held throughout the war. On August 16, 1918, he was commissioned Brigadier General, U. S. Army, and placed in charge as Chief of Chemical Warfare Service, A. E. F.

He was decorated by France with the Cross of Commander, Legion of Honor, October 30, 1918, and received the Cross of the Companion of St. Michael and St. George, of England, June 9, 1919. On July 26, 1919, he was awarded the Distinguished Service Medal.

On March 1, 1920, Brigadier General Fries (now returned to his former rank of Lieutenant Colonel) was appointed Chief of the Chemical Warfare Service, vice Gen. W. L. Sibert, transferred.

Considering its power it has no equal. Physical vigor is one of the greatest assets in any army. Gas, used properly and in quantities that will be easily obtainable in future wars, will make the wearing of the mask a continuous affair for all troops within two to five miles of the front line, and in certain places, for many miles beyond. If it never killed a man the reduction in physical vigor and, therefore, efficiency of an army forced at all times to wear masks, would amount to at least 25 per cent, equivalent to disabling a quarter of a million men out of an army of a million.

But gas does kill and it does wound, in spite of all precautions, and there is every reason to believe that when handled with proper energy and given its legitimate place it will account for 50 per cent of all casualties in future wars.

AMOS A. FRIES, LT. COL., U. S. ARMY, CHIEF OF CHEMICAL WARFARE SERVICE

One great reason why chemical warfare will continue is that it fills a long-felt want on the part of the soldier, that of shooting successfully around a stump or rock. The gas cloud is inescapable. It sweeps over and into everything in its path. No trench is too deep for it, no dugout, unless hermetically sealed, is safe from it. Night and darkness only heighten its effect. It is the only weapon that is as effective in a fog or the inky blackness of a moonless night as in the most brilliant sunshine. Only the mask and the training that go with it protect. Terror, confusion, lack of discipline and control are fatal.

One naturally wonders why the German decided to start the use of gas. A realization of what has just been said indicates his probable line of reasoning. He hoped to win the war in his first powerful onslaught that actually carried him almost to the outer walls of Paris. He wanted first to separate the English and the French and then by holding the French channel ports make it impossible for England to send troops into France, or else force England to transport her troops long distances by sea to western and southwestern French ports. Besides having far longer sea voyages the ships would have been exposed to a hundred times the danger from submarines. His terrific check at the Marne, coupled with the defeat of his later attempt to break through to the channel ports, showed him that the war could not be won at one stroke, unless he could devise some substance or some method of fighting absolutely unknown, and against which there was no protection. Of all things known or ever considered gas alone promised such a result. The date when the Germans began active preparations for the first attack is as yet unknown outside of Germany. It must have been quite early in the war, very probably soon after the battle of the Marne—certainly not later than his repulse in the attack of October 1918, when he strove to drive through to the channel ports.

That first attack was extremely well worked out and successful, from the German point of view. The Allied line was completely broken for a distance of three to five miles, and had the German possessed full faith in his weapon he could have pushed whole armies through that gap before reinforcements had closed it on the following morning. Even with his slowness to take advantage of the break caused by the chlorine cloud, he penetrated so far into the Allied lines as to capture nearly all of the dead and most of the seriously wounded. Thus it happens that the total casualties have never been accurately known. The best estimates place it in the neighborhood of 15,000, of which 5000 were deaths, with only 7000, mostly of the less severely wounded, remaining in the hands of the British.

FIRST BRITISH MASKS

Realizing the fatal effects that might follow a second attack, Lord Kitchener made a dramatic appeal to the women of England and France to furnish cotton pads as masks. So quickly were these furnished that within forty-eight hours the greater part of the front line in the area exposed to attack had the crude protection formed by those pads when dipped in sodium bicarbonate and hypo solution. These pads were insanitary, the solution was often misplaced, and the same individual seldom got the same pad twice.

This was followed a little later by the black veil respirator, in which a larger pad was tied over the face. Some glycerol was added, and the solution lasted longer.

It was reported about this time that the Germans had been seen in a gas attack with hoods pulled completely over their heads. This gave rise to what is known as the P. H. helmet. That is simply a sack made of two thicknesses of flannel cloth with two celluloid eyepieces. It was hot, stuffy, and irritating. However, it furnished fair protection and was all that was available until the small box respirator, the model for all American-made masks, came into use between April and October 1916. This development in the mask situation is thus given at considerable length because of the vital bearing it had on the whole later history of chemical warfare.

As indicated above, the death rate in the first gas attack was probably in the neighborhood of 35 per cent of all casualties—and everybody in front of the wave was a casualty. With the development of masks and methods of training in the use of the mask and in taking advantage of the ground, the death rate fell. At the same time the total number of casualties fell, but not at all in the same ratio as the decrease in the death rate. From a probable death rate of 35 per cent in the first attack it fell to 24 per cent, then to 18 per cent, and, as gas attacks by artillery became general, to 6 per cent, and finally with the extended use of mustard gas the rate fell to 2.5 per cent or less. In the meantime phosgene, five times as deadly as chlorine, had been introduced. Tear gases that forced the wearing of the mask, and thus wore out the physical vigor of the man, came into general use. In 1917 mustard was introduced and a little later the famous German sneezing gas which added to the discomfort and difficulty of protection, by penetrating every mask in common use throughout the war.

DIPHENYLCHLORARSINE AND THE CONNELL MASK

And right here is an interesting story. To the average American who served in France, sneezing gas is only a type of the many failures the Germans made in the war. The gas was looked upon with more or less contempt, and yet it had, and still has, enormous possibilities. This diphenylchlorarsine, or sneezing gas, is twice as deadly as phosgene. Being a smoke or dust it penetrated all masks that depended upon the absorption of gases by charcoal and soda-lime granules as readily as bird shot will trickle through a lot of large-sized broken stone, and in the same manner. It can be kept out only by filters of paper or other materials.

Realizing the possibilities of this gas early in the spring of 1918 those of us in the laboratory and in the field charged with protecting American troops had one of the most anxious periods of our lives. We worked with great haste to develop a filter—and this, first developed by the British and later perfected by the two nations working together, was put into production in April 1918. It took the form of a complete outer covering for the canister that carries the charcoal and chemicals. It added greatly to the breathing resistance, already unduly high. Nevertheless 200,000 were ordered and the majority manufactured, while complete specifications for making them were cabled to the United States and manufacture begun here.

At the same time the Connell mask, the work of an American doctor, was perfected. This mask had a new type canister which inclosed a paper filter that would completely filter out the diphenylchlorarsine. Two hundred thousand of these canisters were also made. This Connell mask is one of the great achievements of the war, and something of which I shall have more to say later. Fortunately the German never succeeded in getting over enough of the diphenylchlorarsine to be dangerous. At the time of our feverish haste in developing this means of protection, we knew how it could be gotten over in quantities that would be terribly dangerous if we could work out the mechanical means of doing so. All of this was communicated to the United States as rapidly as possible, and work pushed here both in getting protection against the diphenylchlorarsine and in developing methods of getting it over. We hoped to beat the German, and we did, and I think that is one of the reasons why he quit when he did. There were other reasons, of course, such as Colonel Wm. H. Walker's hundreds of tons of mustard gas.

MUSTARD GAS

Starting the use of mustard gas in July 1917, the German had the fiendish glee of noting its effect and the number of casualties caused by it for nearly eleven months before he tasted a dose of his own medicine. He told his men that it would win the war, that the Allies had no defense against it, since it burned the body through the clothing as readily as it burned the lungs and the eyes. He told his men that the Allies could not produce it, and in a very large measure he was right. Mustard gas not only produced a tremendous number of casualties, but caused methods of protection to be adopted that were a terrible burden to transportation and a nightmare of discomfort to those using them. The oiled gas-proof suits might be fine for Turkish baths in hot weather, but they were brutal when serving guns in the heat of battle.

Then, too, the Allies had not developed a production of the two ingredients necessary for manufacturing mustard gas by the German method—the only one known prior to the war. While this discovery was a severe blow in the beginning, it turned out eventually to be an extremely fortunate thing for the Allies, as it forced them to develop the now well-known sulfur monochloride method. This in turn enabled them to build up a production that must have been perfectly appalling to the German. That he had some general knowledge of our capacity for manufacturing gas we must assume as certain. We who served in the battle zone through the war got so much information of what was going on in Germany that we knew it was impossible that he was not getting a great deal of the same information from our own country. This information had to be sorted and studied and factors of truth applied, but practice enabled this to be done fairly closely.

FIRST ALLIED USE OF MUSTARD GAS—The French first fired mustard gas against the Germans in the Marne salient about June 18, 1918. From that time the amount of mustard gas fired by the Allies steadily increased, though neither the British nor the American manufacturing capacity was developed quickly enough to get it into the field in noticeable quantities. But the German must have known it was coming. His men had been told the power of mustard gas and dreaded it. When he found it coming back in greater quantities than he sent it over, he had a problem in the psychology of training that he never fully solved. He had taken so much pains to impress his men with the power of mustard gas that he never succeeded in getting them to look upon it as only one of the incidents of war, and one that, while it caused many casualties, would not necessarily be fatal to his campaign.

Mustard gas made a radical change in methods of fighting —not alone with gas, but with other implements of war as well. It forced a change in the mask which the Americans, with open minds and no binding precedents to bother them, were the first to grasp. The wearing of the mask changed from short periods with everybody quiet to long periods in which men had to fight and do their other tasks. Comfort in the mask became all-important. This to the American spelled the doom of the mouthpiece and noseclip, so that we, in France, began work on this problem as early as November 1917.

You have all read accounts of gas attacks, where the gas was always referred to as a cloud. This arises from the fact that gas was first let loose in large quantities from cylinders placed close together. The rapid expansion of liquid chlorine and other liquid gases into true gases caused condensation of vapor, and thus formed the well-known cloud.. At a later date certain smokes, such as tin tetrachloride, were added, because the smoke was irritating and penetrated the early masks in the same manner as diphenylchlorarsine penetrated the later masks.

It was not long until the screening value of the cloud formed by gas began to be appreciated. It was felt that these or similar clouds might be used to screen attacking troops, and enable them to get close to the enemy. This, of course, was not a new idea, but the practical use of the smoke cloud on the field of battle was brought home to those encountering it in gas attacks.

The German after a considerable time hit upon the scheme of generating a non-poisonous smoke cloud and throwing his attacking troops upon the Allies while the latter were wearing the mask. This proved highly successful at first since the English had been taught upon the approach of a gas cloud to adjust their masks and stop all movement. With the coming of mustard gas the formation of a cloud during a gas attack was found not necessary—in fact the absence of a cloud had some distinct advantages. It made the presence of the gas less easy to detect, and that is one of the reasons why the British in the first mustard gas attack in July 1917 thought it was only the ordinary "strafing" of the German. Accordingly they simply took refuge in their trenches and dugouts without putting on their masks, or taking any other precautions against gas. They paid no attention to the pungent smell of the mustard gas, since it caused no discomfort. We can realize the amazement and the extreme anxiety of the officers and medical men and the Chemical Warfare Service when a few hours later men began to go temporarily blind, to get pains in their chests, and to cough, and as the numbers ill rose to hundreds and then to thousands the British realized that a new form of gas had been sprung upon them. Gathering a few duds they rushed them to the field laboratory, 40 or 50 miles away, and soon knew what the substance was, but what the final effects on the men would be was not then known. Severe burns showed on many parts of the body. The eyes in many cases were closed for five to fifteen days. A certain percentage of the men died, whether from the effects on the lungs or from the burns was not known. All this happened just as the British were preparing for their heavy and long-continued attacks against Ypres.

I tell you this in order that you can imagine a little of the feelings of the fellow in the field charged with the responsibility of protecting armies from the enemy's gas, and for developing means for successfully counter-attacking the German with his own gases. It is no disparagement of the British nor of anyone else to say that they held up the date of their attack for two weeks pending further investigations into the effects of this new gas that had little or no smell, no immediate effects, and that burned the body inside and out, thereby producing casualties that later figures showed to be not less than fourteen times as great as were produced by all methods of gas warfare previously known.

NEED OF AMERICAN LABORATORY IN FRANCE

We Americans then began to call for American chemists and an American laboratory to be located in France, where we could get some immediate emergency work done on such problems as mustard gas presented. We never expected to establish in France any considerable research laboratory. We felt that this could be done better in the United States. But we felt, and in this our judgment was sound, that with a reasonable laboratory equipment and a few of the ablest chemists and research men actually on the field in France, we could learn vastly more quickly and better the problems that had to be encountered, and possibly something of the methods for meeting those problems.

An idea that was probably in the minds of many was voiced by a certain officer who made a trip early in 1918 to France and to the front. He said, "You don't need a laboratory here. All you need to do is to state your problems to us in the United States and we will work them out." He forgot that stating a problem is often half solving it, and perhaps more—that to discover and properly state that problem requires greater ability and maturity of thought than its actual solution. A great deal of your research is done by students while working for their degrees, but the man who lays out the work and supervises it is the ablest you can get.

Two short reports of six and two pages, respectively, written by Prof. G. N. Lewis, of the University of California, in the last days of March during the progress of the great German drive against the English, in which he was caught, brought these facts forcibly home to me. He came to me in France as an able chemist, or as one young doctor put it, "one of the best physical chemists in the world." Our laboratory was then just arriving. What to do with him was a question. I sent him to an English Gas Defense School to learn that side of training. He was put in with the Canadians, where he had the fine experience of making his way back for forty miles during the English retreat from that terrible onslaught of the Germans starting March 21, 1918. His two little reports above mentioned showed a military grasp of the situation that I had not expected from a professor of chemistry. They showed that he realized the powers and possibilities of gas, and had the true winning spirit: that the offensive spirit, the spirit that knows that victories are won not by sitting still but by vigorous offensives.

We were then sorely in need of a man to take charge of training the entire American Army in methods of wearing the mask and otherwise protecting themselves from the enemy's gas. Professor Lewis was promptly made assistant on this work and three weeks later put in entire charge. And he made a tremendous success of it. I need only add that this demonstrates the value of having some of the ablest men at the front. A less able man, without a wide knowledge of men, materials and affairs, would not have grasped the significance of the use of gas in that battle as Professor Lewis grasped it, or have been able to take up and devise methods of training and apply them to meet future gas attacks.

What gas did in the World War is such an absorbing topic, and is of such importance that I could talk to you for hours—but I won't. It almost won the war for the Germans in the huge drive above referred to. It caused 75,000 of the 275,000 casualties that American troops suffered on the field of battle, and yet the German used it in a halting and comparatively feeble manner. It is fortunate indeed for us that he never used it on the scale that he might have, had he realized its value and could he have gotten the production of gases that we were getting when the war closed.

SMOKE

Chemical warfare includes gas, smoke, and incendiary materials and they can't well be subdivided. As before stated, all the early gas attacks were in the form of clouds. The value of that cloud, not only for carrying gas, but for screening purposes, began to be realized in the fall of 1917. Clouds of smoke may or may not be poisonous and they will or will not be poisonous, at the will of the one producing the smoke. For that reason every cloud of smoke in the future must be looked upon as possibly containing some deadly form of gas. When you consider this for a moment, you can realize the tremendous possibilities for ingenuity that gas and smoke afford the attacker.

The American, trained for 300 years in meeting nature on her great plains and in her vast forests, was early appealed to by this side of chemical warfare. As early as November 3, 1917, the United States was urged, in a cablegram from the Chemical Warfare Service in France, to push the development of a large phosphorus supply for use as smokes. Not only were the early intuitions of the value of gas borne out by later events, but today the future of smoke appears greater still. The battlefield of the future will be covered with smoke—not the all-pervading black smoke of the battles of the Civil War and of earlier wars before smokeless powder came into use, but a field covered with dots and patches of smoke, big and little, here and there, and everywhere.

Every man who has hunted ducks and been caught in a dense fog with ducks quacking all around, and who has tried to get ducks by firing at the quack in the fog can realize the difficulty of hitting a man on the battlefield when you cannot see him and have only a quack, or less, by which to locate him. The smoke will be generated in candles or two- or three-pound cans that can be thrown out in front of trenches; by knapsacks that can be carried and which will give off dense white smoke in large volume for many minutes; by grenades which while they may be thrown by hand will generally be fired from rifles; by artillery shells reaching 10, 15, 20 miles back of the main battle line; and finally from aëroplane bombs whose radius of action is limited only by the size of the earth. And thus smoke becomes one of the great elements of war in the future. It is more or less wholly protective in its nature; but as it costs more and takes longer to train a man in the various problems involved in modern war than ever before in this history of the world, it is worth while taking every precaution to protect him, once you have him trained.

INCENDIARY MATERIALS

Intimately associated with smoke are the incendiary materials. One of the best of all the smokes is that given off by burning white phosphorus, which is also an offensive agent of first-class power. To me, the bursting and burning of quantities of phosphorus in the field is one of the most difficult situations in the world to imagine keeping cool in, and it certainly proved to be so, so far as the Germans were concerned, in the latter part of the war. This brings me to the point where I want to say a few words about the First Gas Regiment, organized originally as the 30th Engineers.

FIRST GAS REGIMENT

"What's in a name?" is an expression known to every man, and often used. The First Gas Regiment, on the starting of the second battle of the Marne on July 18, 1918, realized what there is in a name. They were organized and known as the 30th Engineers. Now the duties of engineers in war have been known, more or less, for scores of years. The two companies of the regiment were ready to put off a big projector gas attack, but General Foch's counter-attack was launched one day too early. The General Staff immediately put the First Gas Regiment to work on the roads, because they were known as the 30th Engineers. Upon the earnest appeal of Colonel Atkisson, commanding the regiment, they were allowed to go forward and join the infantry in an attempt to take machine gun nests with burning phosphorus and thermite shells fired from 4-inch Stokes mortars. Colonel Atkisson and his officers insisted strongly that they could do this if given a chance; no one outside the Chemical Warfare Service believed they could do it, but as the losses from German machine gunners were becoming exceedingly serious, they were given the chance, and they made good—so good, in fact, that the regiment got little chance to do anything else throughout the remainder of the war. They carried heavy 4-inch Stokes mortars, with their 25-pound shells, for miles, and in many instances kept up with the attacking infantry.

The 4-inch Stokes mortar is a weapon developed by the British for trench warfare and one which they felt could not be used in open warfare. Yet the boys of the First Gas Regiment carried these things and fought with them, and as one infantry officer recently told me, "they were certainly not afraid to go anywhere where they could be of use, whether it was in the front line trench, or in front of the front line trench"—and this last is no exaggeration. In at least one instance in the start of the battle of the Argonne, boys of the First Gas Regiment set up their Stokes mortars out in No Man's Land to establish a smoke screen behind which the attacking infantry could move. But the First Gas Regiment never forgot the value of gas. On the few occasions that presented themselves they used gas and used it effectively.

Then, too, in order to be in on every problem, they developed the use of high explosive in Livens projectors. This projector, I might say, is the simplest gun known, being a straight drawn steel tube closed at one end, and from 2 ft. 9 in. to 4 ft. in length. It fires a bomb carrying 30 lbs. of liquid gas or high explosive a distance of a mile—a distance that in the future will be increased to at least a mile and a half. They were fired in large numbers simultaneously by being connected up with electric firing batteries, and were exceedingly effective, whether with high explosive or gas. Indeed they provided the method of gas attack most dreaded by the Germans.

For a moment just consider what was done at the attack on Lens in the spring of 1918, an attack participated in by the first two companies of the First Gas Regiment. On that occasion 2500 of these 60-lb. drums, filled with phosgene, were dropped on the enemy at one time, in the middle of the night. The concentration of gas in such attacks is terrific, the detonation of the bursting bombs is terrifying, and the war proved that none but the most highly disciplined soldiers could stand up under the strain of these attacks. But projectors were difficult, slow, and laborious to install. Our efforts in those days, as they will be in the future, were to make these attacks mobile, much easier, and consequently of far greater frequency.

The Gas Regiment in the St. Mihiel battle fired on the Côte des Esparges one hundred of these high explosive bombs at the zero hour on the morning of the attack. That hill, famous for its strength through four years of struggle between the French and Germans, disappeared completely as an enemy strongpoint. Nothing remained but torn and broken barbed wire, bits of concrete pill boxes and trenches filled with debris, and a few scattered fragments of clothing.

The gas troops will, in the future, handle all short-range methods of firing gas, smoke, or high explosive. They will deliver the greatest quantities of material possible up to ranges of a mile and a half or a mile and three-quarters. So effective and so efficient are these short-range methods of projection that the No Man's Land of the future will be the width covered by these projectors and mortars. They can't, and never will, compete with the artillery, where range and great accuracy are the most important factors. The efficiency of artillery gas shell, or artillery smoke or high explosive shell is only one-fifth that of the projector. Hence for economy and efficiency the artillery will be used to fire gas, smoke, high explosive, and incendiary materials only at ranges beyond those reached by the gas troops.

So greatly were these possibilities appreciated in the summer of 1918 that the number of gas troops authorized for use against the Germans was increased from 6 companies to 54. Back of all this, however, was the productive capacity of the United States which insured that those troops would be able to fight day and night, summer, winter, and fall until the war was over. No wonder the German quit—it was time, and he knew it.

COÖPERATION OF CHEMISTS

Interesting as is this discussion of work of the Chemical Warfare in France, it must be dropped now to give a few moments to the discussion of the future relations of the Chemical Warfare Service with the chemists and the chemical industries of the United States.

That relation must be one of whole-hearted coöperation. The Chemical Warfare Service cannot be a success unless the chemists of America back it; unless they are willing to coöperate with it as they did in the war. If they will do that, the United States need have no fear of any future struggles.

WORK DURING THE WAR—Neither the history of the World War nor, indeed, the history of any other war, shows such whole-hearted, enthusiastic coöperation of professional men as was shown by American chemists during the World War. Starting under Dr. Manning, of the Bureau of Mines, at the American University, and at numerous colleges and research institutions throughout the United States in February before the war began, the organization grew until the Research Division alone contained 1200 technical men and 700 service assistants. Its work covered exhaustive research into over 4,000 different materials.

FUTURE RESEARCH IN THE CHEMICAL WARFARE SERVICE—The Government cannot afford, and we do not believe it would be advisable, to attempt an organization of even one-tenth of this size to operate in peace-times under the Chemical Warfare Service. The Chemical Warfare Service must maintain a small research organization. There will be certain lines of investigation that can best be carried on there, or lines which no other institution desires to touch upon. The Chemical Warfare Service must have enough trained men to tell, at least tentatively, whether a new idea, a new substance, or a new method, can probably be successfully adapted to chemical warfare. This will involve, in large measure, a thorough understanding of military problems, military organization, and military methods. We shall expect to be experts in that and to be ready at all times to take up any and every question that you, from the four corners of the United States, may submit to us. We want your ideas—all of them. If something comes to us which has been proven impractical or impossible, we shall courteously tell you why the idea is unusable and will request you to submit others.

The thousand research men that are working throughout the United States as compared with every one that the Chemical Warfare Service can maintain will certainly bring forth 75 to 90 per cent of all the new ideas, materials, and methods for use in chemical warfare. We hope that you will be able to make researches along certain definite lines that the War Department may ask you to pursue. We hope that we shall be able to keep in such close touch, and work in such full coöperation with the chemical industries of the country that the magnificent plant at Edgewood Arsenal may soon be a thing of the past. We do not believe the Government should attempt to manufacture poisonous gases on a huge scale. Many of these gases are now proving useful and even large factors in commercial processes. We hope to keep in such touch with the various chemical industries that we can count upon this one and that one all over the United States to produce within a given number of days on the outbreak of war, a given quantity of gases. We believe that in this way we can build up, more quickly and to a greater extent than by any other method, the necessary large output of poisonous gases required in a war with a first-class power. When that time comes the great government plants will be abandoned. Our Edgewood plant should be capable for at least five years, with moderate upkeep, of being put into large-scale production without notice. By that time we hope to have worked out with the chemists, the research institutions, and the great chemical industries a plan for utilizing all chemical resources, men, and factories in less than 30 days after the outbreak of war. We believe that if this is done satisfactorily it will be one of the greatest possible guarantees of future peace.

The universal adoption of gas warfare on sea and land and in the air, combined with its persistent quality, will make that nation able to produce and use gas in the largest quantity superior in war to any other nation on the globe. The United States can reach that position and maintain it, and I believe that we are going to get such encouragement from the War Department that we can do it. I feel sure that the Army appreciates the value of chemical warfare, and that it appreciates also the value of the chemists to chemical warfare.

The German had forty years of chemical research and development before the war and he had over two years of swift chemical development in the war before the Americans started in. With a lack of foresight which I trust will never be evidenced again in America, we had done nothing to meet the chemical warfare activities of the Germans. We entered the war, then, in 1917, with as big a handicap as could be imagined, but through the energy and coöperation of the chemists, we not only, in 1918, overcame that lead of forty years and more, but we surpassed it, so that in the end we led Europe not alone in quantity of manufacture, but in research, in training, and in actual gas tactics on the field of battle.

The war taught us conclusively that what may be a tremendous success in the test-tube in the laboratory may be an utter failure in the field. Hydrocyanic acid gas, called "Vincennite" by the French, is a brilliant example. Instantly fatal in high concentrations, it has almost no serious effects in concentrations appreciably below the fatal one. Hydrocyanic acid, being known to be so fatal, was at once seized upon by the Allies, and particularly the French, as a great battle gas; and notwithstanding it was such a complete failure, there are even yet writers on chemical warfare and chemical matters who are not aware of the fact, as shown by the following quotation from a French writer on chemistry in the war. He stated that two French professors discovered a gas "which produced instant mortal action, but which our chiefs, from an excess of humanitarian scruples, which were indeed superfluous, decided not to employ." What an error! It was employed in hundreds of thousands, perhaps millions, of shells and the Germans thought so little of it that in a memorandum to the German armies they stated that the French gas, meaning Vincennite, was harmless, except in the concentrations in which the Germans themselves used it to kill vermin.

TRIBUTES TO INDIVIDUAL CHEMISTS

Right here I want to say a few words of praise and appreciation of the chemists who served with me in France. You all know pretty well the names of those who pointed the way to successful chemical warfare over here. Each of you knows of Walker and McPherson and their coworkers who created at Edgewood Arsenal the greatest chemical plant in the world.

You all know of Burrell, Kohler, W. K. Lewis, Bancroft, Lamb and a score of others who made the American University the greatest research organization ever dreamed of.

You know of Dewey and his five and a quarter million American-made masks; of Dorsey and his Development Division at Cleveland, and scores of others who did work equally as brilliant though in less prominent positions. But how many of you know the story of Major Karl Connell?

Major Connell was not a chemist by profession, but a physician in New York City. Before the war he had won considerable fame by inventing masks for administering anesthetics. As said before, he was not a chemist, but he had a large store of practical chemical knowledge. His name was handed to me in France as that of an energetic, able man who had served several years with the 71st Regiment, National Guard of New York. I cabled for him, and he reported early in November 1917. I had intended to assign him to training; but when, in the first hour of our interview, I had elicited from him a statement as to his work on anesthesia, I showed him models of all masks in use by the Allies and the enemy and told him that we felt that we must eventually have a fighting mask; that while we had adopted the English mask this was simply because it was the best in existence and we believed in using what was available, though at the same time we also believed in starting investigations toward the ideal. After another hour's work with these masks he said he believed he could make a new one embodying the principles of clear vision, comfort, ease of adjustment and foolproofness—that is, a mask that would be easy to put on and difficult to disarrange and one that could be manufactured economically on a large scale.

I sent him to Paris where in three weeks he produced the first model. Though it was crude he had faith enough in it to try it in a high concentration of chlorine. It leaked a little but the general result was so satisfactory that I sent him to England to complete his work. I consider his first model a marvel, inasmuch as he did it in a strange city, speaking a language foreign to him, and working with a tinsmith who knew no English. His work was continued in England under the most trying circumstances. Doubters and even scoffers called him everything but a genius and a wise man, but he persevered, and by the first of March 1918 had produced the first all-American mask that was then, and is to-day, a complete protection against all known gases. It embodied the principles of the latest type American mask that was not perfected until nearly eight months later. Its principal features were pressed metal facepiece, sponge rubber to make a gastight fit between the face and the mask, a canister carried on the back of the head, the omission of the mouthpiece and noseclip, and the bringing of the inspired air over the eyepieces so as to keep them clear.

Sent to the United States in July to take up the question of producing this mask, he was told that the sponge rubber could not be made successfully here and that a mask with a fabric facepiece was being developed which would be superior to his. He dropped his own development and threw his whole soul into the problem of developing what is now the 1919 American mask, the finest mask in the world.

His reward?—no promotion, no medals, not even a citation—only the proud feeling of a man who did all that he could for the cause and who won the love and undying admiration of those who knew him as I knew him.

Then there was G. N. Lewis, of whom I have already spoken, Professor of Chemistry in the University of California, who stepped from the quiet of the university into the maelstrom of war in one of the greatest battles of history, and won in the Chemical Warfare Service a recognition of greatness equal to that which he possesses to-day in the field of chemistry.

Then there was Colonel Zanetti, a teacher of chemistry and a master of the French language, who reported to me in the middle of October 1917. Feeling the urgent need of closer contact with the French, he was at once assigned as Chemical Warfare Service Liaison Officer with them. He did a tremendous work in cementing cordial relations between the French and American Chemical Warfare Services and was allowed to delve deeper into French secrets than any other foreigner living.

Then there was Goss, of Princeton, young, energetic, with a considerable knowledge of the Army gained in the National Guard of New Jersey. Arriving in France about the middle of October he was assigned as Chemical Advisor and put to work coördinating the chemical information we were getting. Not satisfied with doing only two or three men's work, he proceeded to get into the field—in touch with the British, to hunt Germans in No Man's Land, and eventually to rise to be Chief Gas Officer of the Second Army and one of the best experts on chemical warfare.

There was Colonel Hildebrand, also of the University of California, who progressed so rapidly in the military application of chemical warfare problems that he was put in command of the Proving Ground and the American Army Gas School, a position he filled with the greatest credit to himself and to the United States.

Another was Major Keyes, of the Boston "Tech," who got together in the United States, transported to France, and there put up and operated one of the finest laboratories in all Europe. The work of that laboratory was small in comparison with the work done in American University, but it was vital and would have become vastly more so had the war continued another year. The emergency problems in the field—such as the determination of when the chemicals in the canisters were destroyed, and the opening and determining of the contents of new gas shells—were problems looming bigger and bigger all the time.

Then there was Major Pope, a chemical engineer, whose report on the impossibility of our manufacturing gases in France was timely, correct, and vital. Up to that time certain persons contended that Americans must manufacture their gas in France and must fill their shells there. His lucid report on the impossibility of doing that work stopped all such talk and kept the United States from embarking on an impossibility.

There were many others in the field and in the laboratory or on the proving ground who did all that man could do in their positions and thus contributed powerfully to winning the war. Among them I want to mention just one more name—that of Captain J. E. Mills, of the First Gas Regiment. Joining that regiment in the United States, he was among the first to reach France. Given many opportunities to go into the laboratory or on duty at headquarters, he always begged to stay with the regiment. He stayed there even to his own detriment, so far as promotion was concerned.

He was one of the mainstays of Colonel Atkisson in all his work, giving his entire strength and very nearly his life to the cause. In his loyalty to the regiment regardless of danger and hardships when even more important work under pleasanter conditions was offered him, he typified the best in American manhood. All honor to him and to the unsung thousands like him who suffered and risked all that "Liberty might not perish from the earth."

FUTURE OF CHEMICAL WARFARE

The future of chemical warfare has been pretty well indicated by what has been here said in regard to its use in the past war and its possibilities as the Chemical Warfare Service sees it. Gas is too deadly, too dangerous, too easy to develop and produce in secret for any nation to afford to give it up.

There have been many stories of super-gases invented in America or elsewhere, that even in small quantities would wipe out whole armies. No such gas was produced in the war. No such gas will be produced. A gas may be discovered that will penetrate existing masks, and unless mask development be such as to stop the gas, the result will be disastrous to the army encountering it. It is the business of the Gas Defense side of chemical warfare to prevent just such conditions. It met and solved all such problems in the past war, and I have no doubt that it will meet and solve such problems in the future. If it can't, we are lost—lost, because, while I have the greatest faith in human nature, I would not risk the lust for power and wealth that the future United States might engender in other peoples if the latter felt they had a substance that could wipe out our Armies as fast as they approached. That all the world is feeling this way about chemical warfare is indicated by the following quotations. The first one is from a statement of the Under-Secretary of War for England, when appealing to Parliament for funds to carry on chemical warfare. He said, in part:

> So long as there is any danger of other nations continuing these methods of warfare, research and experiment in chemical warfare must be pursued. Research must not only be directed towards the gases and apparatus likely to be employed in the future, but also towards protection against all possible gases. Training in the use of gas will be confined to appropriate branches, but training in defensive measures will include the whole army.
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> We must continue our studies of what is known as chemical warfare. No nation has renounced the use of poison gases as the result of the Peace Conference. There are nations whose word we could not respect if they did renounce it. It is essential to study the offensive side of the chemical warfare if we are to be prepared for defense. The great importance of adequate defensive appliances arises from the fact that preparations for the offensive use of gas can be made in peace-time with great secrecy, and may have far-reaching and even fatal results in the early stages of a war.
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> ....For these reasons it is necessary to make adequate provision for research, experiment, and design in connection with war material. It is equally necessary to avoid overlap, duplication of effort, and the setting up of military institutions for scientific research which can better be done by existing civil institutions. It is our policy to farm out to civil scientific institutions all pure research that can profitably be farmed out, and, generally speaking, to restrict military institutions to applied research and the preliminary design of apparatus.

Another quotation is taken from a statement by General Debeney, Director of the French College of War. This statement first appeared in the United States in the March 20 issue of the *Pittsburgh Dispatch*. Among other things General Debeney said:

> Should war begin now, aviation, and especially gas, would play one of the most important parts. The progress of aviation would make the rear of each front, and very far in rear, extremely dangerous, and the progress of chemistry would permit the use of gas on zones of such an extent as cannot be imagined.
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> Making gas is naturally rapidly done, because all the manufacturies of chemical products—still so numerous in Germany—can be requisitioned, but to make airplanes is much slower.
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> The defense against gas seems to be more difficult than against airplanes. I believe that against airplanes, the anti-aircraft artillery is susceptible of making rapid progress, and perhaps in that very instance gas will be one of the best ways, if with appropriate shells the *air can be poisoned all around the attacking airplanes*. It would be much more effective to create, for example, a sphere of poisoned air a mile around the airplane, instead of trying to hit the machine directly with bits of the shell.

Finally, the following statement, taken from the *Des Moines Register* of March 22, 1920, probably expresses about as well as any words I have yet seen the position that I believe the average man in the United States takes regarding chemical warfare.

> As to poison gas, we would as well accustom ourselves to the thought that it is now a permanent and important part of war. To get hot about that is as futile as to scold the men who invented gunpowder, and is on the same plane. It is ridiculous to declaim about the incidentals of war while ignoring the truth that war itself is the enemy. If America ever again "draws the sword," to use an expression that shows the difference between war of yesterday and war of to-day, America will go in with as much reliance on gas shells as her antagonist can possibly have. Nobody in the military councils at Washington or West Point even dreams of anything else. And if America does not add a few refinements to the use of gas it will be because American wit and ingenuity have broken down, which isn't likely.

VICTORY AND ITS RESPONSIBILITIES

By Charles H. Herty

Editor, Journal of Industrial and Engineering Chemistry

A half decade ago the common lament among men of our ilk was that the science we represent and its applications were not appreciated by our fellow-citizens. We had grown accustomed to and accepted as almost ineradicable the popular conception of the chemist as a long-haired, bespectacled individual performing some mysterious magic in a carefully secluded workshop. We fretted over the grotesquely distorted reportorial accounts in the press of any matter pertaining to chemistry and our eyes looked in vain for intelligent and sympathetic discussion of the chemist's work on the editorial pages of the American press. Salaries were inordinately low and the general atmosphere surrounding the profession was such as to repel rather than attract the students in our universities.

To-day that state of affairs no longer exists, the American chemist has come into his own. Chemistry is on the lips of everyone, the real personality of the chemist is understood and his work is appreciated at its true value. A victory has been won—a victory over public opinion. What are the evidences of that victory?

In the offices of the SOCIETY's News Service are thousands of newspaper clippings, the number mounting daily, from every section of the country. The clippings from the news columns show reasonably scientific accuracy, combined with an approved popular style of presentation which makes them readable for the masses of our people, while those from the editorial pages show a sound and far-sighted grasp of matters chemical.

In the bookshops there are large sales of popular books on chemistry. Men like Ellwood Hendrick and Edward Slosson have made splendid contributions. In the Senate gallery lately I happened to be sitting in the section just above the desk of Senator Knox of Pennsylvania. During the "morning hour" while a multitude of minor measures were being considered, I observed the Senator deeply engrossed in reading a book. What book do you suppose it was? Not a work on international law, as might have been expected—no, it was Dr. Slosson's book, "Creative Chemistry," and the Senator was so delighted that he needs must share his pleasure, so he took the book to Senator McNary, evidently with a warm recommendation, for the Senator from Oregon immediately wrote a memorandum of the title and the publisher. Could that have happened five years ago?

Another evidence is the matter of salaries paid young chemists. The head of one of the greatest research laboratories of the country told me just a few days ago that two years ago men just graduated from colleges with the Bachelor's Degree were paid $18 per week. In that same laboratory they are now paid $34.

Five years ago but little was heard of industrial chemical research. Now the number of laboratories devoted to such work is legion and constantly increasing. Empiricism in industry is steadily giving way to scientific control and development.

But undoubtedly the strongest evidence of victory won is the sympathetic attitude of the present Congress toward all measures affecting the chemist and his work. I am a thorough believer in the idea that our Congress is truly representative of our people and its present friendly disposition has its roots in a similar feeling on the part of the "folks at home."

Five measures affect favorably our work one of which is now a law; the other four have been passed by the House of Representatives and are now before the Senate, three with favorable reports from Senate Committees and one doubtless soon to receive an equally favorable report.

That measure which is now a law is the National Prohibition Act. In view of the past uniform policy of including a visit to a brewery in the list of plant excursions at our General Meetings some of you may be taking exception to the mention of this act as one affecting favorably the work of the chemist. In explanation, however, let me ask how many of you are aware of the wording of the title of this act? Here it is: "An act to prohibit intoxicating beverages, and to regulate the manufacture, production, use and sale of high-proof spirits for other than beverage purposes, and to insure an ample supply of alcohol and promote its use in scientific research and in the development of fuel, dye and other lawful industries." That title is the mandate of Congress to the Bureau of Internal Revenue in framing its rules and regulations for the carrying out of the act. And the Bureau has faithfully carried out the expressed purpose of Congress. Both the Congress and the Internal Revenue Bureau have leaned toward the chemical industries in the drafting of the law and in the administrative procedure thereunder. Tax-free "alcohol may be withdrawn * * * for the use of any scientific university or college of learning, any laboratory for use exclusively in scientific research, or for use in any hospital or sanatorium." Pharmaceutical and medicinal manufacturers have been aided by a modification of the act of 1906 which defined tax-free denatured alcohol to be such as "destroys its character as a beverage and renders it unfit for liquid medicinal purposes." The present act requires only that the denaturing "render the alcohol or any compound in which it is authorized to be used unfit for use as an intoxicating beverage." Previously certain formulas for denaturing were set up by the Government and the manufacturer had to utilize whichever of these most nearly suited his needs. Now, however, if a manufacturer finds no suitable formula for denaturing he can demand such from the Government. Surely chemists have abundant grounds to be thankful that Congress in drafting this legislation which gave the knock-out blow to alcohol as a beverage nevertheless kept clearly and sympathetically in mind the importance of alcohol as a chemical reagent. A copy of Regulation No. 61 of the Bureau of Internal Revenue of the Treasury Department should be on the desk of every chemist.

Then there is the Longworth Bill for the safeguarding of our coal-tar chemical industry. You are familiar with its details and you thoroughly understand the character and the source of the opposition it has met. I shall never forget the look of consternation on the faces of two of the leaders of the German dye industry last October when during a conference there was brought into the room a copy of the *Frankforter Nachrichten* containing the announcement that the Longworth Bill had passed the House of Representatives. That news told them clearly that the American people were determined to make themselves forever independent of any foreign nation for such supplies, and it required no superhuman effort for them to guess which particular nation was in mind. Their gloom, however, was somewhat lightened when I explained to them that the bill had still to pass the Senate. Will it pass that body? I have always believed so, and in confirmation of that belief let me read to you an extract from a telegram I received from Senator Watson, in charge of the bill, just before leaving New York:

> I earnestly hope for the passage of the dyestuffs bill as reported from the committee. A widespread propaganda is being engaged in by opponents but I feel sure that the measure that passes the Senate will fully protect the American dye industry and thereby give an impetus to industrial and engineering chemistry in America.

But this was not all of Senator Watson's telegram, he adds:

> Trust also that the bill for the protection of surgical instruments and chemical glassware will soon become a law in order to stimulate an additional interest in these subjects in the minds of the American youth, particularly those who attend our colleges. I assure you I am doing everything in my power to secure the enactment of these measures.
>
> (Signed) JAS. E. WATSON

Plainly the Senator is in complete accord with the Council of this SOCIETY which voted in favor of the repeal of the duty-free importation clause and which unanimously recognized in this privilege a most dangerous channel for insidious propaganda among those who some day will constitute the chemical personnel of this country. The Bacharach Bill has a deep significance for chemistry.

Another measure affecting directly the work of the chemist is the Nolan Bill, which seeks to strengthen the forces and increase the activities of the Patent Office. For years it was impossible to arouse public interest in this matter, but a few weeks ago a public hearing was held on this bill. The result was its speedy appearance on the House calendar with a favorable committee report. Its passage by the House with only one dissenting vote is a fitting example of the cordial attitude of the Congress.

Of deepest importance, however, is the feeling in Congress toward the Chemical Warfare Service. In the face of the minimizing efforts of those highest in authority in the War Department, the House of Representatives has already voted that this Service shall be an independent unit in the new army. The bill is now being debated in the Senate, and the Senate Committee on Military Affairs has taken an even stronger attitude in behalf of the Service than did the House. Just three days ago I received the following telegram from Senator James W. Wadsworth, Jr., chairman of the Senate Committee on Military Affairs.

> You know, of course, that the Army Reorganization Bill already passed by the House of Representatives provides for the maintenance of a separate Chemical Warfare Service in the War Department. The Senate Bill now under discussion in the Senate also provides for a separate Chemical Warfare Service. The Senate Committee on Military Affairs was thoroughly convinced that the Chemical Warfare Service was of such vast importance that it should be allowed to develop its possibilities under its own officers and with the invaluable assistance of the chemists of the country rather than be merged in some other service of the Army in which it would inevitably occupy a secondary position out of all proportion to its real importance. In view of the action of the House of Representatives and similar action by the Senate Committee it is fair to assume that the legislation when finally completed will provide for a separate Chemical Warfare Service.
>
> (Signed) JAMES W. WADSWORTH, JR.

The future of the Chemical Warfare Service is assured. Let us in turn respond to this action of the Congress and give to that Service that loyal support which will insure America's leading the world in chemical warfare.

There is only one regret in this situation, the removal of Major General Sibert from the head command of the Chemical Warfare Service. This action by the authorities of the War Department was a distinct shock to the country. As an aggressive organizer of that Service, General Sibert had won the high regard and affection of the members of the Service and of civilian chemists. He had been unwilling to avail himself of the privilege of retirement at will, granted by Congress in appreciation of his work on the Panama Canal, and had determined to remain on active duty until the future of the Chemical Warfare Service was fully assured in the reorganization of the Army by Congress. From the outset he advocated fearlessly and convincingly the continuation of the Service as an independent unit of the Army, and his views prevailed, though they were in marked opposition to his superiors in the War Department. And he paid the price, and was removed from the head of the Service. Now comes the news of his voluntary retirement. A man who played so conspicuous a part in the construction of the Panama Canal, and who assured to this country the future of the Chemical Warfare Service can well afford to rest upon his laurels. He will carry with him always the best of good wishes from the chemists of America.

It was fortunate that the only logical successor of General Sibert was Lt. Col. Amos A. Fries, whose work as head of this Service with the American Expeditionary Force had demonstrated his fine ability and proved him thoroughly equipped for this important position.

With such evidences of victory over public opinion before us, the question naturally arises: How has this been accomplished? It is needless to say that war activities in the past few years have brought the chemist to the attention of our entire people. Upon the successful outcome of investigations and their translation into large-scale production depended the lives of our soldiers and the task was worthily met. Then, too, the revelation in the early days of the war of our economic dependence in the matter of dyes and medicinals, of chemical glassware, of optical glass, chemical porcelain, and of scientific instruments cut deep into the very life of many of our most important industries. Dependence does not belong to the American make-up, and the speed with which this dependence was removed both as to quality and quantity of output made a story of amazing wonder. But it was necessary that that story be told and told in language that could be understood in order that the work should receive due recognition. Here it is that the chemist has worked a revolution within himself.

There was a time when the chemist felt that it was no business of his that interpretation of his work should be given in everyday language. His concern was with the day's work in the laboratory and there his responsibilities ended. So, too, he felt that as an organized group he was not called upon to express an opinion on matters of chemical economics. I remember well at the Council Meeting in Seattle in 1915 when the suggestion was made that this SOCIETY should urge legislation which would insure a domestic dye industry there was so much opposition to the SOCIETY'S so expressing itself, on the ground that it was an economic rather than a chemical question, that the matter was laid over until the following day. Fortunately the tide turned at that time and vigorous resolutions were passed which marked the beginning of the fight for an American industry.

Since that day this matter of interpretation of chemistry to the public has gone forward by leaps and bounds. Believing that we ourselves were responsible for the neglect on the part of the daily press, prominent chemists made up their minds to meet the press half way, and by their personal efforts furnish material which reporters could make into attractive stories for their papers. This material was greedily accepted by the press. Still there was a lack and this was filled by securing the services of an experienced newspaper man, Mr. John Walker Harrington, who worked daily with the chemist in this matter of interpretation. The officers of the SOCIETY realized that the question of public education as to the real meaning of chemistry to the nation was essentially a function of this SOCIETY. Funds have been appropriated in steadily increasing amounts as the work has progressed. The details of the operation of this News Service have been eagerly sought by representative organizations here and in other lands. The success of the work is due solely to the one fundamental thought that we have striven to promote nothing but the welfare of our country through a better comprehension of chemistry. In an autocracy such as Germany was, chemistry was fostered by its ruler. In a democracy such as America is, we are seeking to foster chemistry through popular education and upon this sure foundation it will last.

Another form of public education which is developing is that of public addresses by chemists to non-technical audiences. I was deeply interested a few weeks ago in reading in a New York paper a lengthy account of an address by our former President, Dr. Julius Stieglitz, before the Fashion Art League of America and the Alliance of Art and Industry on the subject of "The American Dye Industry." Those who know Dr. Stieglitz's delightful method of presentation can readily understand the pleasure and profit of his hearers, but my chief pleasure lay in the fact that Dr. Stieglitz in the midst of his busy life found time and had the disposition to make such an address. He has set an example which should be followed by each of us.

Another powerful factor in public education as to chemistry has been the National Exposition of Chemical Industries. Originating amid predictions of failure, it soon demonstrated its useful public function. In that Exposition the chemist has taken the public into his confidence and furnished the opportunity for public inspection, not only of the products of the industry but of the crude natural resources from which and the machinery by which these products are manufactured. The character of the attendance at these annual expositions is illustrative of the widespread interest in chemistry and of the eagerness with which people will listen to the story of the chemist when it is attractively told.

What have been the results of this victory over public opinion?

Capital has been attracted to the chemical field in constantly increasing quantities. According to the statistics of the New York *Journal of Commerce* the authorized capital of new chemical, drug, and dye companies during the past five years was as follows:

1915	$ 65,565,000
1916	99,244,000
1917	146,160,000
1918	73,403,000
1919	112,173,000

while the total for the first three months of 1920 is $60,188,000. This great influx of capital has increased the demand for chemists and with this has come increased remuneration for the chemists' services. These conditions have attracted chemistry students in numbers which five years ago would have been incredible. The chief result of this victory, however, is the increased prestige which the chemist has gained. The legitimate feeling of gratification over such an outcome is not based upon complacent self-satisfaction but upon increased opportunity which is afforded for further service.

Such a victory as has been won carries with it distinct and increased responsibilities. It would be a mere platitude to say to you, fellow chemists, that this new atmosphere brings to each of us inspiring cause for even more earnest effort. What I do want to leave in your minds is that in such a sympathetic atmosphere men can work with hope and freshened zeal, in the feeling that their work is being recognized in its true significance. I need not say more about this, because I think we all grasp that point. But, gentlemen, as we work in our laboratories we must show that same spirit of originality, of fearless willingness to break into new lines, to open new paths, that characterized the spirits of our pioneer forefathers. The old fetish of a certain foreign superiority in chemical matters is gone. America's day is coming! America's day in chemistry is coming, but it is not yet here in its full realization. The one responsibility that I want to bring home to you to-day is that of carrying on still further this question of public education. It is the same story I have just been talking about. I have painted the rosy side of the picture, but there is much yet to be done. We can't be satisfied and feel that our work is thoroughly understood in this country when two such institutions as Cornell University and the Massachusetts Institute of Technology formulate plans and offer the facilities of their laboratories, their equipment and their staffs, to the War Department, and have the War Department write back: "We don't need any chemistry in this matter (referring to preparations for war)." Yet that is exactly what happened in the spring of 1917. Of course, soon afterwards they woke up, and then began a general scramble. Now is the time for education and general understanding of chemistry to be completed.

In a much more recent time than three years ago when we went into the war, even within the past six months, there has been put forward by the Secretary of War a proposal to build a great engineering school down in the woods of Virginia, a twenty million dollar institution, and send down there graduates of West Point, who have had fourteen weeks of chemistry, give them a year's training, and let them do the research work for our Army in all the problems of chemistry which pertain to warfare. You laugh, but that is to my mind one of the most suggestive of thoughts, that so intelligent a man as the Secretary should have, at the close of this war, such a hazy idea of what it takes to make a research chemist, and should seriously make that proposal. And General March says we don't need any Chemical Warfare Service, because there isn't going to be any more chemical warfare. Those are the gentlemen at the head of the War Department. I don't know whether they are educated yet. General Sibert and Colonel Fries have gone strongly the other way and put this thing right, anyway it looks now as if it is right. That is the situation to-day in spite of five years of education.

We talk about chemistry being prolific around New York City. There are hundreds of chemical industries there, and 2,000 chemists in the New York Local Section, and rafts of them over on the Jersey flats, yet when the mayor of that great city appointed his Committee on Defense and announced that he was putting on it representatives of all the interests centered in and around New York there wasn't a chemist within a mile of it. A little while later the governor of New York appointed another war committee consisting of representatives of the various industries. I went through the list carefully to find out which one of the boys was on the committee, and I am still looking for him.

With all that has been said in the papers, in the magazines, before committees of Congress, in both the Senate and the House, in spite of the fact that the President of the United States has twice selected a certain specific industry—the coal-tar chemical industry—and urged upon Congress favorable legislation in its behalf, there was introduced in Congress on the opening day of the session of last year, a bill to protect further that industry, and that bill is not yet a law!

Public opinion is not so organized, not so active in behalf of chemical matters that it will immediately spring up and react favorably upon Congress. What happened the other day when the Appropriations Committee of the House brought in a report cutting the items of the Bureau of Foreign and Domestic Commerce, cutting out the commercial attachés, and limiting the work of the Bureau? What happened? Within twenty-four hours business organizations in every section of the country were pouring telegrams and sending committees into Washington, and that appropriation went back to normal size, and passed. That is what organized sentiment can do. In marked contrast was the action of Congress in severely cutting the appropriations requested by the Bureau of Standards, whereby the splendid work of that important scientific bureau will be badly hampered in the future. Scientific men have not rallied, as did the business organizations, to the support of that bureau which contributes so much to their interests. I believe that Congress represents and desires to represent the people of this country, and yet an industry which has such tremendous ramifications and deep-seated significance to this country from so many standpoints, as testified to by men in the Army, in the Navy, in the Administration, and by workers outside of the industry itself, waits restively for the passage by the Senate of a bill which has been favorably reported by Republicans and Democrats alike with no trace of partisanship about the measure. Why has not this bill become a law? Because public opinion hasn't awakened.

One other matter—at the National Exposition of Chemical Industries there have been shown from year to year the results of the efforts of the railway companies to utilize more and more the chemist in making chemical surveys of natural resources; in other words, the chemists were doing the work of industrial agents. But right now those laboratories are closed. An officer of one of the railroad companies stated recently that he doesn't know whether they can ever get started again, that all records have been lost or destroyed, all specimens are gone. They have nothing to exhibit at this year's Exposition. When an important movement like that can be completely wiped off the boards we haven't yet taught our people fully what chemistry means to them.

Here is another thing. When the expedition was being assembled to go to Paris to represent America in the formulation of the Peace Treaty there were brought together men from nearly every line of American effort. They were going to negotiate a peace with a nation which was primarily a nation of chemists, whose work was so well known to all, for the lack of whose chemical material we had suffered in this country in the early days of the war—and yet, how were the chemists of the country represented on that mission? I don't know Mr. Summers personally. He has never been a member of the AMERICAN CHEMICAL SOCIETY. He has never been at our meetings. He has never published any articles in chemistry journals. He was first heard of down in Washington representing chemical matters on the War Industries Board. We do know him somewhat and somewhat unfavorably in connection with our platinum conservation program for munitions manufacture. Mr. MacDowell I know and am personally very fond of, but he doesn't pose as an organic chemist. He is in the fertilizer business, but he isn't a chemist and doesn't profess to be. As days went along, in came Mr. Baruch. He's been a lot of things, but I never heard him called a chemist. I wrote a little squib once in the JOURNAL, about a new use for the ultramicroscope: to find among the members of the Peace Commission someone who knew anything about chemistry. With the exception of Alonzo E. Taylor, a food chemist, I stick to that statement. If public education as to chemistry had been further advanced such a situation could not have arisen.

Our work affects the national security. It is up to us to make sacrifices, to answer the call of that man right there, the Chief of the Chemical Warfare Service, Colonel Fries, whom we hope soon to call again General Fries, it is up to us to meet him quick with the best we've got. It isn't his work, it's America's work, and the chemists of America must meet that responsibility in every way. I want to quote the words of one of the most prominent industrial dye chemists in Germany, a remark made to a group of members of the Inter-Allied Commission which visited Germany soon after the armistice. Some of you met him over here at the Eighth International Congress, Dr. Duisberg. Speaking about the Peace Commissioners in Paris, he said in words to this effect: "They are going to make a hard treaty for us. We have got to accept it. You beat us on production in this war, but we are going to beat you on production in the next war." "In the next war"—that is our responsibility to this country.

And then remember this. Before the Ways and Means Committee in Washington last spring Mr. Francis P. Garvan, the Alien Property Custodian, was testifying in behalf of the American dye industry. It was just a few days after the first dirigible came to this country from the other side. Mr. Garvan drew a graphic picture of what might be expected within a few years, outlining the possibility of a type of enemy dirigible carrying poisonous gases, flying across the ocean, and wiping out the city of New York in a few minutes. Some said he was overstating the danger. And yet Colonel Wm. N. Hensley, Jr., of the Air Service, gave out only the other day a statement made public by the War Department regarding the scheduled plan of the Germans for Thanksgiving Day, 1918. I'll read it:

> * * * the German effort was scheduled to take place about Thanksgiving Day, 1918, and that the L-72, which he described as the "largest airship in the world," was expressly constructed for the raid, measuring 775 feet from tip to tip and equipped with six engines of 260 horsepower each. The L-72 was capable of carrying five tons of high explosives and incendiary material.
>
> Action for every hour and minute of the trip was foreseen. Every possible contingency of weather, fuel exhaustion, damage to ship or machinery failure had been reckoned. Weather charts of the Atlantic were gathered, files of the German Admiralty were combed and the records of the merchant marine were searched.

That was on the schedule for the latter part of November 1918, fortunately just two weeks after the armistice was signed. Mr. Garvan spoke of a possibility, but it has now been disclosed that it was a positive intent scheduled in every detail. The Germans had already planned for this conquest.

Now I want to say a word to you about this same gentleman, Mr. Francis P. Garvan. I think he is the strongest ally that the chemists of this country have. It has been my good fortune in an unofficial capacity to be associated with him for the last three years while he was Assistant Alien Property Custodian, and later Alien Property Custodian, in working out the ramifications of this German network of intrigue, and as president of the Chemical Foundation, in straightening out this patent tangle which has troubled us so much. I received this telegram from him last night:

> Please convey to the members of the AMERICAN CHEMICAL SOCIETY my sincere appreciation of the great work performed by them in the recent war. This war was essentially a chemists' war and the initiative, energy, and self-sacrifice on the part of the chemists of this country was, I feel sure, more than any other one thing responsible for the success of America. As a result of this victory the responsibilities of the American chemists have become increasingly greater. We now look to them to make America the leader of this industry in the world. We expect them to excel all other countries in the development of explosives, gases, and the other things necessary in warfare. We expect them to lead the world in the development in industrial chemistry so that the commercial supremacy of our country can be assured. We expect them to excel the Germans in the manufacture of dyestuffs so that never again will America have to depend upon Germany or any other country for these most importtant products. A great responsibility rests upon the chemists of this country. Long and patient research work and the building of more plants will be necessary so that the American chemists can fulfill the obligations which now rest upon them, responsibilities of our victory in the recent war. The American people are alive to and sympathetic with the work of the chemists of this country. I for one believe that within a very short period America will lead the world in chemical research work. We are only a short way from that goal now. I want to see America the greatest chemical and dyestuff country in the world and I know that every member of your SOCIETY does too.
>
> (Signed) FRANCIS P. GARVAN

Now, gentlemen, I want to read finally one extract in further introduction to you of the personality of Mr. Garvan. It is the conclusion of his testimony before the Senate Finance Committee. I do this because there is a thought in it which to my mind is one of the most inspiring which has been brought forward by a public man, at least as affecting our work.

> Gentlemen, Dr. Albert and Bernstorff reported to their government that America could never establish the dye and pharmaceutical industry in this country, as we lacked the moral power for the creation of such an industry; that her each party pursued its own selfish interests, but nobody kept the whole in mind; that this problem could only be solved through regard for all points of view, and that the conflicting selfishness of this country rendered that solution impossible. Wrong; wrong; as ever, wrong! Let them await the answer of American patriotism, American sacrifice, and American ability.
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> We felt that we would like to be a part in the taking of the forces of science developed by them—which they have only turned to the desolation and destruction of mankind—and placing them in the hands of what we believe to be a higher and purer civilization, to see if we cannot, out of the terrible mess of this war, do something constructive with these same scientific forces, do something to direct them into the channels of alleviation and helpfulness to humanity. It is only to give American principles and character a chance that we ask you to hold these people off until we get our education. Then we can meet them without any tariff.

To my mind that puts the goal before us. That elevates our work far above mere commercialism. What in the world does it mean to make dyes, to make sulfuric acid, to make caustic soda? We need them, they are a part of our civilization, and the men who are in the industry are entitled to a just return, but, my fellow chemists, there is a higher mission ahead of us. It is foreseen in Mr. Garvan's statement, though he is not a chemist. These other things must of course be done and done well, but, oh, my friends, the chemistry of the body is too little known. Think about the fact that the body is a mass of chemical reactions, which when normal mean life, and health, and happiness, but when abnormal signify disease and misery and unhappiness. Yet these are simply chemical changes. This country is spending millions of dollars for drugs on the bare chance that they may happen to be the right thing. We must get these matters on a scientific basis. We must get deeper into the knowledge of how these drugs act. It will take time, and a tremendous amount of research, but surely the goal of American chemists is a noble one, if it can start toward the attainment of the alleviation of the suffering of America. What lies beyond that we do not know, perhaps a prolongation of the average life of mankind, perhaps more happiness through life. There is something deeper in our work than mere commercialism. I am talking about industrial chemistry now, too. I don't know exactly what it is. I can't yet get my thoughts clear about it, but down in my heart I believe that when our people thoroughly understand what we are trying to do, and are thoroughly sympathetic with our aims and aspirations, when full opportunity is given for the highest energy and effort of American chemists, somewhere in that science to which we devote our lives will be found that which is uplifting to life in every way.

COLLOID SYMPOSIUM

SOME PRACTICAL APPLICATIONS OF COLLOIDAL CHEMISTRY

By Jerome Alexander

Ridgefield, Connecticut

"COLLOIDAL" FUEL

What promises to be one of the most far-reaching advances made under the stress of the recent war, when necessity literally was the mother of invention, is the discovery that by means of a suitable "fixateur" or peptizing agent and suitable treatment, very large percentages of cheap tars and finely powdered coal waste may be dispersed in fuel oil with a sufficient degree of permanence to enable the mixture to be stored, piped, atomized, and burned practically like fuel oil itself. Since this new composite fuel will at one stroke relieve the drain on the earth's rapidly diminishing stores of petroleum, as well as lead to the efficient utilization of all kinds of coal waste (culm, screenings, dust), inferior fuels (peat, lignite), and even cellulose waste (slabs, sawdust), it may be hailed as a powerful factor in the conservation of our natural resources and a lasting benefit to mankind.

Realizing the vital importance of the Allies' oil supply in the conduct of naval, military, and manufacturing operations, the German submarines bent every effort to destroy tankers; and Marshal Foch is said to have cabled America: "If you don't keep up your petroleum service, we shall lose the war." While the Allies' navies were dealing with this peril in a most decisive fashion, Lindon W. Bates, head of the Engineering Committee of the Submarine Defense Association, with the assistance in laboratory matters of Dr. S. E. Sheppard and other chemists of the Eastman Kodak Laboratory, courteously opened to him, developed a colloidal fuel, which, by practically doubling the usefulness of every oil cargo, would have of itself materially assisted the defeat of the Hun efforts.

Coal or other combustible solid is prepared for dispersion by being pulverized so that about 95 per cent passes through a 100-mesh, and 85 per cent through a 200-mesh screen. This of course means that by far the greatest weight is in particles hundreds and thousands of times larger than colloidal dimensions. But we should remember that the violent motion of the colloidal particles causes the Brownian movement of much larger particles, as is the case in milk where the fat globules can be seen in the ultramicroscope oscillating about under the ceaseless bombardment of the casein ultramicrons. It has been found that a fluid fuel may be made containing as much as 40 per cent by weight of powdered coal, and mobile pastes containing up to about 75 per cent; and mobile gels may be made both from the liquid and the pastes.

The exact nature of the fixateur is withheld pending the issuance of patents here or abroad, but it is stated that ordinarily between 0.5 and 1.5 per cent of the essential component of the fixateur is used, whereas about 0.1 per cent exercises a noticeable influence. The amount is determined by the nature of the mixture, the components, and the degree of permanence desired. The bulk of the particles does not begin to settle until the period of "life" has passed, the colloidal fuel having a limited "life" which may be regulated to meet requirements—days for power plants, weeks and months for ocean-going vessels and central storage stations. Heat and agitation revivify the liquid fuel, and the paste form may be kept for years.

Being heavier than oil or even water, colloidal fuel compresses in a unit volume the maximum thermal value, thus economizing storage space; and it may be stored under and extinguished by water, thus avoiding evaporation, deterioration, and fire risk. Its operative efficiency is high, for when sprayed into the hot fire box the oil-permeated particles of carbonaceous matter are still further atomized by the sudden gasification of their imbibed oil. It possesses the advantages of fuel oil over coal—absence of smoke, dust, and ash, practical elimination of labor in loading into storage space and in firing, with resultant saving in time for "coaling" and for raising steam. As with oil, a protective smoke screen may readily be produced by over-firing, and the fire is subject to instant control.

SMOKES

While it is an ancient principle of strategy to attack an enemy under cover of natural fog or mist, the recent war resulted in an enormous development of artificial smokes as aids to naval and military offensive and defensive operations. Like the cuttlefish, steamers strove to escape pursuing submarines in colloidal clouds of their own making, and soldiers crept to the attack under the protection of a smoke barrage. In the air, nature's own clouds were favorite hiding places for aëroplanes and dirigibles, and the latter (especially Zeppelins) often produced their own concealing clouds.

In times of peace the treatment of smokes and fumes is mostly confined to their coagulation by the Cottrell process, by which sulfuric acid mist or zinc oxide fumes have been collected as part of the ordinary course of operations, and by which injurious industrial dusts, *i. e.*, smelter and cement fumes, have been converted into sources of profit. There is, however, one case of the commercial production and utilization of smoke that possesses features of interest—the use of the so-called "smudge-pot."

Smudge-pots are burned in orchards, especially in spring or early summer, when weather conditions indicate that the tender blossoms or fruit are apt to be injured by frost. The heat emitted by the pots is apparently a small factor, their efficacy being due to the dense clouds of smoke evolved by the burning smudge oil. This remedy is of course useless in very cold weather, and serves only to prevent what agriculturists term a light frost, which has for its precursors a still, clear atmosphere, and a temperature approximating the freezing point. No frost of this kind occurs on cloudy or windy nights.

The freezing process, in the absence of smoke, seems to proceed as follows: as the temperature drops, moisture deposits like dew upon leaves, fruit, buds, and other surfaces furnishing nuclei, and congeals into ice crystals or "frost," when the slight heat thus set free by condensation is dissipated into the surrounding cold atmosphere, the freezing being also facilitated by the evaporation of part of the deposited water. The smoke, however, furnishes throughout the entire lower atmosphere innumerable nuclei for the deposition of moisture, and the slight but widely distributed heat thus liberated is sufficient to carry the temperature, locally, above the freezing point. Moisture on such small nuclei does not readily evaporate, and the smoke fog furthermore forms a kind of protective blanket which reflects terrestrial heat and prevents its dissipation.

SHOWER-PROOFING OF FABRICS

Ordinary textile fabrics are readily wet by rain, but if coated with a surface film of wax or the like (aluminum stearate), the falling droplets roll off "like water off a duck's back." This water-proofing effect is readily understood if we consider the interfacial surface tensions involved:

1—Surface tension water/air, denoted by σWA
2—Surface tension water/fabric, denoted by σWF
3—Surface tension air/fabric, denoted by σAF

Practically speaking, the surface attraction of the untreated fabric for water is so great (*i. e.,* σWF is so small[1]) that both the surface film or skin of the raindrop and the air film on the fabric are burst; the raindrop spreads itself out on the fabric, and is absorbed into its pores. That is, wetting occurs if

$$\sigma WF < \sigma WA + \sigma AF \text{ or } \sigma WA > \sigma WF - \sigma AF.$$

In the case of the treated fabric, σWF is very much increased; becoming in fact the surface tension water/wax, for surface tension is only skin-deep. Therefore $\sigma WF > \sigma WA + \sigma AF$ or $\sigma WA < \sigma WF - \sigma AF$ and no wetting takes place.

FLOTATION

The understanding of what happens in flotation will be much simplified, if we bear in mind that, notwithstanding the presence of many disturbing and variable factors, there are two main triphasic systems involved. These are:

1—Ore/water/oil, from which the true ore (usually a sulfide) must emerge with a film of oil which enables it to be taken up by the air bubbles and thus floated with the froth, while the gangue is wetted and flowed off at a lower level.

2—Air/water/oil, which yields the bubbles to float the oiled sulfide.

Denoting

1—Surface tension water/oil by σWO
2—Surface tension oil/sulfide by σOS
3—Surface tension water/sulfide by σWS

the oil will then distribute itself over the interface water/sulfide (*i. e.*, the sulfide will be oiled) if $\sigma OS < \sigma WO + \sigma WS$ or $\sigma WO > \sigma OS - \sigma WS$.

In the second system denoting

1—Surface tension water/air by σWA
2—Surface tension water/oil by σWO
3—Surface tension air/oil by σAO

the oil or some of its constituents distribute themselves at the interface water/air because

$$\underset{75}{\sigma WA} > \underset{23}{\sigma WO} + \underset{33}{\sigma AO} \quad \text{(approximate values).}$$

This yields air bubbles with a more or less stable surface film, *i. e.*, a foam or froth. This film is miscible with the oil film on the sulfide, although not necessarily identical with it, because there may be a separation of the constituents of the oil by differential adsorption. The oiled sulfide particles therefore act like oil, and, distributing themselves at the interface water/air, are attached to the air bubbles and lifted to the upper froth layer, if they are not too heavy or are not knocked off.

In the foregoing no account has been taken of complicating factors which are always present and while space will not permit an exhaustive discussion of them and their results, the most important will be considered.[1]

WATER—Here are found dissolved air, crystalloids, and colloids. The dissolved air aids in bubble formation by reducing the internal pressure of the water. For the most part the crystalloids, especially *acid* electrolytes, act beneficially, being adsorbed by and coagulating the fine slimes, clay, etc., which then tend to repel the flotation oil, recalling the old-fashioned household expedient of moistening the mouth and throat with orange or lemon juice before taking castor oil, and thus avoiding the taste. Some electrolytes, especially alkalies (*i. e.,* Na_2CO_3) in small percentages, are powerful deflocculators, and by reducing the surface tension water/oil and water/sulfide tend to emulsify the oil, wet the sulfide and deflocculate the slimes. Humic substances, especially when converted into alkali salts, and protective colloids generally, act in like manner—the injurious effects of glue are well known. Colloidal clay or very fine gangue act similarly—"fat" clays will emulsify oils, coal tar, and asphalt.

ORE—Outside of soluble impurities which dissolve in the water, the fineness of grinding is most important. The gangue should be fine enough to flow off, but not so fine as to cause the undesirable effects just referred to above. If the sulfide particles are too large, the air bubbles cannot lift them, or they are easily knocked off; if they are too small, there is a great loss in efficiency, for the surface of the bubbles may be satisfied by a layer of small particles which represents a small weight of sulfide.[2] The results may also be adversely affected by the surface oxidation of the sulfide.

OIL—This is deserving of the most intensive study, since it is the factor most readily controlled. Moreover, the great and sudden development of the art of flotation has turned the various oil markets topsy-turvy, necessitating a constant search for new oils or combinations not only from financial considerations, but also because of actual shortage in the supply. Since conditions are different at each plant, and since different lots of ore even from the same mine may vary, a careful study is necessary to determine what oil or mixture is best, and also to know how to meet changing conditions. Particularly useful will be a determination of the foam-producing factor as opposed to the sulfide-oiling factor.

LUBRICATION

The consumption of petroleum is increasing so rapidly that a material decrease in the supply, if not actual exhaustion, lurks in the not far distant future. W. B. Hardy in a trenchant paper[3] has shown that we may with confidence look to colloid chemistry to aid us in finding the lubricants of the future.

Glass surfaces selectively adsorb from the air rather more of the atmospheric impurities than of the elementary gases and water vapor, yielding a film about 1 $\mu\mu$ (1×10^{-7} cm.) thick, which Lord Rayleigh termed "grease" because it has the general properties of an oil.[4] For this reason a new or raw glass surface has different mechanical properties than a satisfied or neutral surface.

It is not possible to get a raw surface[5] of glass. One cannot cleave glass; but the "grease" film may be removed by rubbing the surface under water. Soaking is insufficient; actual vigorous rubbing is necessary, preferably with the finger tips until a peculiar clinging feeling is produced: the same which is felt when the edge of a finger bowl is rubbed so as to give out a musical note. A surface cleaned in this way has some remarkable mechanical properties, the most striking being that two cleaned surfaces seize when pressed together with a relatively small force. This may be demonstrated very simply by measuring the tangential force needed to produce slipping. That true seizing occurs is proved by the tearing of the surfaces which takes place in the act of slipping.

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[1] It should be borne in mind that the surface tension *decreases*, as the attraction between the phases *increases*. In fact, when the positive surface tension in a two-phase system becomes zero, solution may take place.

[1] Mechanical agitation and temperature exercise considerable influence. Callow estimated that with four different oils, three oil percentages, two pulp densities, and two temperature changes, there are about 60,000 possible different combinations of conditions.

[2] The layer of tiny adhering ore particles forms an armadillo-like armor about the air bubbles, which to a large extent protects them from coalescence and destruction.

[3] *J. Soc. Chem. Ind.*, **38** (1919), 7*t*.

[4] This adsorbed layer of "grease" tends to make pipettes and burettes deliver inaccurately, so analysts remove it by oxidation with bichromate.

[5] Raw surfaces are readily made by cleaving mica, and if immediately put together again, they adhere so strongly that they withstand a powerful lateral pull, and usually tear the surface when finally separated. [J. A.]

The function of lubricants is to keep the applied surfaces in the neutral condition by maintaining a "grease" film on each. Not all fluids, however, can act in this sense as lubricants for any particular surface such as that of glass. Water, ether, alcohol, benzene, and strong ammonia are apparently entirely incapable of maintaining a lubricating film on glass. Seizing occurs just as readily when they are present as it does with cleaned surfaces. Glycerol differs from the fluids mentioned above in the fact that though it will not maintain a lubricating film it does prevent seizing when present in excess. For instance, the maximal tangential force which a pair of cleaned surfaces would support without slipping was measured in grams, 55. Flooding the surfaces with water, benzene, alcohol, etc., left this value unchanged. When a film of glycerol was deposited on the surfaces the force still stood at 55, but it fell to 9 when the surfaces were fully flooded with glycerol.

The expression "film" used above denotes a layer of fluid on the solid surface of the order 10^{-7} cm. in thickness. With a true lubricant the facility for slipping is maximal when a layer of such excessive tenuity separates the solid faces and nothing is gained by increasing the thickness of the layer. Thus with castor oil the weight required just to start one face of glass slipping over another was 10 g. when only the invisible film of fluid mentioned above was present, and it was still 10 g. when the surfaces were flooded with oil.

Some fluids indeed seem to lubricate better in thin than in thick layers; that is to say, to act in the contrary way to glycerol. Acids as a class behave in this way, the solid faces again being of glass.

PULL IN GRAMS

	FILM	FLOODED
Acetic acid	40	47
Sulfuric acid	37	47
Oleic acid	10	13

If this result can be fully substantiated it will be an important and striking physical fact likely to throw much light upon the process of lubrication. One broad conclusion emerges from these facts, namely, that lubrication depends wholly upon the chemical constitution of a fluid, and the fact that the true lubricant is able to render slipping easy when a film of only about one molecule deep is present on the solid faces, suggests that the true lubricant is always a fluid which is adsorbed by the solid face. If this be so, then the problem of lubrication is merely a special problem of colloid physics.

Some solids, notably graphite, are lubricants themselves. But the chief function of graphite seems to be as an aid to lubrication by oil. The graphite is disintegrated in the bearing and besides filling up relatively large imperfections, its colloidal particles are adsorbed by the iron, forming in reality a graphite surface which has a lower surface tension against oil than iron has. Practically this means that the oil film adheres more strongly to the graphitized surface and therefore needs greater force or pressure to break it down; *i. e.*, the bearing will stand greater speed and pressure. Acheson's "oildag" consists of a paste of colloidal graphite dispersed in oil. A small percentage is mixed with the lubricating oil and feeds with it through the finest orifices. "Aquadag" is the corresponding water-soluble product, stabilized with tannin.

CERAMIC PROCESSES ASSOCIATED WITH COLLOID PHENOMENA[1].

By A. V. Bleininger

PITTSBURGH, PENNSYLVANIA

This paper is intended to present some of the aspects of colloid chemistry which have a bearing upon the technology of clays. Within the scope of this contribution it is not possible to consider the subject at all completely and attention can be called only to certain of the more important topics.

Clays are mixtures of finely divided hydrated aluminum silicates with granular matter such as quartz, feldspar, mica, etc. These represent all grades of subdivision, from the coarsest to the finest. The property of plasticity, the ability of the substance to be molded when admixed with water and to retain the shape imparted to it, is to be attributed to the dispersed state of the aluminum silicates, principally $Al_2O_3.2SiO_2.2H_2O$, known under the general term of clay substance. The pure type mineral, known as kaolinite, sometimes found in crystalline form, rarely occurs in clays but has usually been reduced to particles apparently devoid of crystalline structure, of the magnitude of 5μ or smaller, admixed with colloidal material like ferric oxide and organic matter and frequently stained by absorbed salts. Clays are not necessarily plastic in the natural state but may have been indurated by pressure or heat, or set through other agencies so they cannot be made plastic without the aid of grinding. This is particularly the case with materials consisting of hydrated silicates other than $Al_2O_3.2SiO_2.2H_2O$, such as halloysite, pyrophylite, indianite, etc.

The colloidal character of clays was recognized as early as 1874 by Schloesing[1] and later more definitely by Rohland[2] and Cushman,[3] and it was agreed that a clay is very plastic, fat or sticky when the colloid matter is in excess or sandy; weak or non-plastic if the granular matter predominates.

The colloidal characteristics of clays are substantiated most effectively by ultramicroscopic examination. Recent work of Jerome Alexander[4] has shown that the Brownian movement is observed with practically every type of clay suspended in water, varying from the rapid motion of the finest particles to the more sluggish one of the larger particles or aggregates or when hampered by the presence of electrolytes.

CLAY SUSPENSIONS

Clay suspensions in the deflocculated state when filtered through paper will show decided turbidity in the filtrate. Again, such a suspension, after the coarser portion has been allowed to settle out, will give rise to the familiar phenomenon of the Tyndall cone upon passing light through it.

Clay suspensions are affected in a very pronounced manner by various reagents, both electrolytes and non-electrolytes. Probably the first striking phenomenon observed in this respect is that of absorption. Upon adding solutions of salts like NH_4Cl, $BaCl_2$, $Al_2(SO_4)_3$, and $CuSO_4$, an appreciable amount of the basic ion is absorbed but practically none of the acid ion. Thus Sullivan[5] found that 1 g. kaolin absorbed between 0.0038 and 0.0169 g. of CuO from 50 cc. of a solution containing 2 g. of $CuSO_4$, but was itself slightly dissolved. Cushman[6] found the absorption of NH_4 from NH_4Cl to be 0.077, of Ba from $BaCl_2$ to be 0.373, and of Al from $Al_2(SO_4)_3$ to be 0.075 per cent after standing three days and using 0.1 N solutions.

Deeply colored solutions of metallic salts may thus be decolorized by passage through clay. Organic salt solutions like malachite green or methylene blue, consisting of large, complex molecules are absorbed to a very striking extent, and in fact Ashley[7] employed the magnitude of absorption of the former as a measure of the colloid content or the plasticity of clay, using a solution containing 3 g. of the dye per liter. This type of absorption follows the general exponential equation with fair agreement.

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[1] Published by permission of the Director of the Bureau of Standards.

[1] *Compt. rend.*, **79** (1874), 376, 473.

[2] *Z. anorg. Chem.*, **31** (1902), 158; **41** (1904), 325.

[3] *Trans. Am. Ceram. Soc.*, **6**, 65; Bureau of Chemistry, *Bulletins* **85** (1904) and **92** (1905).

[4] Private communication.

[5] U. S. Geological Survey, *Bulletin* **312**.

[6] Bureau of Chemistry, *Bulletin* **92**.

[7] U. S. Geological Survey, *Bulletin* **388**; Bureau of Standards, *Technologic Paper* **23**.

Salts as a class tend to coagulate clay while bases deflocculate it, as is common with all dispersed materials. This type of reaction is of considerable technical importance. Thus the action of NaOH, Na_2CO_3 or Na_2SiO_3 in increasing the dispersion of the clay particles brings about a decided decrease in the viscosity of the system and, hence, according to Stokes' law makes possible a sharper and more prompt separation of the granular matter and the clay substance proper, a fact made use of in the washing and purification of kaolins, first proposed by Keppeler.[1] The clay thus treated and separated must later be coagulated with acid or salts to render possible its filter pressing.

Another industrial application of the deflocculation of clays is connected with the so-called casting process in which the constituents of a porcelain or other ceramic body are stirred with water containing about 0.3 per cent of Na_2CO_3 and Na_2SiO_3 in terms of the dry weight of the clay materials, to form a thick but still readily fluid suspension. Here the addition of the alkaline reagents is effective in reducing the water content required to keep the mass in the liquid condition. In fact, the amount of water present is not greater than that found in the same mixture in the plastic state without the use of the alkali. This phenomenon may be readily demonstrated by adding to a plastic mass of kaolin a small amount of Na_2CO_3 or NaOH. It will be noted that the plastic material is suddenly transformed into the fluid state. Upon the addition of acid or a salt like $Al_2(SO_4)_3$ it will revert to the plastic condition, thus illustrating the effect of deflocculation and coagulation. In casting, the clay suspension is poured into a plaster mold which absorbs a sufficient amount of water to cause the mass to solidify into a layer conforming to the outlines of the mold.

On the other hand, coagulating reagents, acids, and salts are used to increase the plasticity and strength of certain clays and to thicken suspensions of glazes and enamels.

All the phenomena of deflocculation and coagulation occur in phases. Thus the addition of alkali to a clay suspension brings about first a decided viscosity minimum, followed by alternating maxima and minima until finally the phases merge in a definite direction. Similar conditions prevail also in a coagulation series with the phases in reverse sequence. Schulze's statement that the coagulating ions apparently increase in effectiveness proportionately with their valence is confirmed in the work with clays. Certain organic substances like the tannins react upon clay suspensions somewhat like the alkalies, though with less sharply defined phases. They may also assume the function of a protective colloid in that they render the clay less sensitive to the action of electrolytes. Kaolin suspensions are easily affected by the presence of impurities, and impure clays containing soluble sulfates deflocculate only with difficulty or not at all.

The fluidity of clay suspensions is probably the best means of following changes taking place in clay-water systems and for this reason technical viscosimeters have been used frequently for the estimation of the deflocculating or coagulating effect of reagents. While this practice is perhaps justified for suspensions containing a large excess of water it is not warranted for heavier ones, and the criticism of Bingham[2] that such mixtures show evidence of viscous flow is justified, since the volume of the flow varies directly as the pressure. It would seem then that viscosimeters of the Bingham type should be preferred for measurements of this kind even though the technical instruments suffice to mark the maxima and minima which it is necessary to establish. However, even such determinations of the viscosity or its reciprocal, the fluidity, of clay suspensions suffice to establish the relative plasticity of different clays inasmuch as equal concentrations will show fluidities inversely proportional to the general plastic nature of the materials.

One of the most interesting phenomena observed with clay suspensions is the electrical deposition of the particles by a direct current upon the positive electrode against the flow of water away from it. This is the basis of the invention of Schwerin for removing clay from positively charged particles (iron bearing minerals) and depositing the former upon a metallic belt or revolving drum. The addition of small amounts of sodium hydroxide increases apparently the charge of the clay particles and facilitates their deposition.. As a matter of fact the separation is effected far more completely by previous washing treatment with the use of sodium hydroxide for bringing about maximum deflocculation. The principal application of the Schwerin process consists in the deposition of the material upon the moving positive electrode, thus replacing the filter press just as in the electro-osmose filtering apparatus devised by the same worker. It seems that the migration velocity is that of the heavier ions and that the voltage determines the degree to which water has been eliminated.

These several phenomena of clays in the suspended state have been explained as being due primarily to the negative charge of the clay particles, so that the introduction of negative or OH-ions will bring about further dispersion or deflocculation and that of H-ions coagulation. It is apparent, however, that the case is not one of mere electrostatic repulsion or attraction. The presence of salt solutions not only brings about a change of the charges on the particles or neutralization but also a host of possible and complex interactions more or less complete as, for instance, in the addition of sodium carbonate to a clay already carrying absorbed calcium ions, and hydrolysis. Ashley compares these reactions with those of soap in that in either case we are dealing with a weak acid, only slightly soluble, the salts of which are all hydrolyzed and with the exception of those of the alkalies and ammonia but difficultly soluble.

PLASTIC CLAY

Clay in the plastic state likewise possesses some interesting properties most of which still require further elucidation.

The measurement of plasticity itself has not been possible up to the present time except by empirical or indirect means, and it is only recently that progress has been made in this direction.

The simplest mechanical conception of plasticity would be to consider it a case of viscosity according to the relation $d = KW$, where d = deformation, W = load, and K = constant. It seems, however, from the researches of Bingham that this is not the case but that we must differentiate between viscous and plastic flow in that the yield point of the former is zero and of the latter finite. In a diagram correlating pressure with volume of flow the curve of a viscous liquid will pass through the origin and in the case of a plastic substance we have an intercept on the pressure axis. In the case of clays studied by the writer[1] the pressure required to start initial flow through an orifice 0.25 in. in diameter varied from 40 to 75 lbs. per square inch according to the character of the clay. With decreasing water content the pressure required to produce flow increased very rapidly, and on the other hand with increasing amounts of water it dropped, so that the resulting curve was hyperbolic. Atterberg[2] has made use of the conception of flow and lower plasticity limits. He determined the amount of water required to just cause flow of the clay and also the water content at that stage where it can barely be rolled to form threads. The difference between these values he calls the plasticity number. Kinnison[3] has found this factor to be quite characteristic, though he considers that it should be plotted against the water content of the plastic clay and the resulting diagram used for the classification of the different materials.

The plasticity of clay is, without doubt, greatly affected by the presence of organic matter, humus, tannins, etc., and it seems to be a fact that acidity is conducive to the greatest development of this property. The aging of clays does indeed improve their plastic working quality and it is believed that this is due in part to the formation of organic acids, caused by bacterial action or chemical processes. The addition of small amounts of reagents like Al_2Cl_6 to kaolins brings about similar results provided the material is stored for some time, but no change is observed with the more impure materials. Tannic acid shows this action in a more marked degree.

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[1] *Z. angew. Chem.*, **22** (1909), 526; Bureau of Standards, *Technologic Paper* **23**; Bureau of Mines, *Bulletin* **128**.

[2] Bureau of Standards, *Scientific Paper* **278**.

[1] *Trans. Am. Ceram. Soc.*, **16**, 392.

[2] *International Reports on Pedology*, **1911**.

[3] Bureau of Standards, *Technologic Paper* **46**.

Alkalies, on the other hand, are quite active in inhibiting the plastic quality of clays to a very pronounced extent. Electrolytes in general affect clays in that they increase or reduce the water required for the development of the plastic state and also the shrinkage upon drying. This effect depends obviously upon the kind and quantity of the salts already held by the materials and, as a rule, the purer clays are influenced to a greater extent than the more impure ones. Thus, upon adding up to 0.05 per cent of $NaCl$, $CaCl_2$, and Al_2Cl_6 to Georgia kaolin the volume contraction due to drying was reduced by about 1.0 per cent. Here again the first small additions of the reagent show phases indicated by maxima and minima which gradually disappear as the concentration is increased. With most clays, the salts, chlorides, and sulfates increased the water content and drying contraction.

DRYING SHRINKAGE

In the drying process itself we have the contraction in volume of the plastic clay as a typical property of colloid materials which may show a magnitude of as high as 100 per cent, or as much as the true volume of the clay itself. The drying shrinkage is thus in a measure a criterion of the colloid nature of the clay, being the greater the more pronounced this development is. The presence of electrolytes affects not only the magnitude of the contraction in drying but the capillary flow of the water through the clay as well. Thus it is well known that the addition of sodium chloride in small quantity will accelerate the passage of the water to the surface and thus lessen the strain imposed upon the clay in drying.

Upon drying clay and rewetting, it does not seem to recover its original plasticity at once and this is the more pronounced the higher the temperature to which it is carried. The retempering of the dried clay is associated with evolution of heat. We are dealing therefore with a case analogous to that of a "set" gel, and a change which becomes irreversible at a given temperature, usually at about 500° C., unless subjected to treatment with steam at high pressure.

It is interesting to note, likewise, that the drying shrinkage is the greater the more slowly evaporation of the water is allowed to take place, and vice versa.

FIRING OF CLAY

In the firing of clay two points are of special interest during the early periods of the process, the expulsion of the hygroscopic and the chemically combined water. The removal of the former leaves the clay in a state exceedingly sensitive to the presence of water vapor and gases, absorbing them with great avidity. This condition is accentuated after the evolution of most of the chemically combined water, when the material becomes an even better absorbent, taking up eagerly sulfur dioxide and trioxide. In this state it possesses marked catalytic properties, as in the oxidation of sulfur dioxide to trioxide, the formation of ethylene, etc. It is possible that this characteristic of dehydrated clays may find uses in the technical application of a number of chemical reactions. This material shows considerable activity also when ground together with calcium oxide and moistened, producing a cement of good hydraulic setting qualities.

The dehydration is necessarily endothermic and is associated with a decided increase in molecular volume. Upon further heating of the clay an exothermic reaction takes place at about 900° C. which may be associated with an irreversible change of a colloidal nature, or the dissociation of the aluminum silicate, perhaps into $Al_2O_3.SiO_2$ and silica.

As the firing temperature is raised the external clay volume contracts, especially in the presence of fluxes, due to the effect of surface tension until the heat intensity is sufficient to bring about practically complete closing of the pore space. It is said then that the clay has become vitrified. With increased softening of the mass its lowered viscosity permits the surface-tension effect to become more and more prominent until finally the original shape has been lost and the surfaces curved analogous to the formation of a drop of water from a melting fragment of ice.

In the case of clay products the process, of course, is not allowed to proceed as far as this and the firing is stopped when the desired degree of vitrification has been reached, while with glass it is allowed to continue. At the same time the density of the vitrified or fused silicate decreases with increase in temperature, irrespective of the external contraction.

The relation between temperature, time, and contraction in volume is therefore a very important one and expresses the result of the heat work done. It enables us to represent graphically the progress of condensation or vitrification and is equally important in the study of the firing processes of carbon, alumina, zirconia, thoria, etc.

Although surface tension is probably the most important factor in bringing about the condensation of the substances with which we are here concerned, vapor pressure[1] undoubtedly enters into the case in dealing with substances showing a vapor tension sufficiently high or in the admixture of inert materials with those of a more volatile character. Thus, the comparatively high vapor pressure of magnesia at temperatures considerably below its fusion point is instrumental in bringing about its earlier condensation. Formation of sillimanite from kaolin and alumina may be brought about at about 1500° C. by the addition of a small quantity of boric acid, and the cementation of carbon from coal is likewise made possible by the presence of volatile constituents.

In all the silicate reactions at higher temperatures diffusion through the semi-rigid mass plays an important role.

Finally, wherever the chemical composition and the heat treatment permit it the end result is the partial elimination of the colloid phases and their replacement by crystalline identities. Thus, the clay substance decomposes into sillimanite and silica, glass yields calcium silicate, and cement its several calcium silicates and aluminates, but there is invariably present a residuum of an isotropic matrix.

REPORTS

REPORT OF COMMITTEE APPOINTED TO DEFINE THE FIELD COVERED BY RESPECTIVE DIVISIONS AND SECTIONS OF THE AMERICAN CHEMICAL SOCIETY

The Committee Appointed to Define the Field Covered by Respective Divisions and Sections of the AMERICAN CHEMICAL SOCIETY has carried on correspondence with reference to the questions submitted, and now begs to report as follows:

1—It is believed that the designations which have been adopted for the different divisions and sections are themselves sufficient definitions of the field to be covered in each instance.

2—It is recommended that the established procedure of the SOCIETY shall be to give authors their choice of the division or section in which they are to present their papers whenever it is possible to do so. The Secretary of the SOCIETY shall be empowered to assign the papers to other divisions or sections in case the paper is obviously out of place or when in his opinion it will be to the advantage of the division or to the program in general so to assign it.

3—When submitting the titles of papers authors must indicate something of the discussion to be given, which might influence the proper placement of the paper. The title only in some cases is not sufficient indication, since a given subject may be discussed from any one of several angles, each one of which might place it before a different division of the Society.

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[1] E. Podszus, *Sprechsaal-Arch.*, No. 1, 1912.

Authors are required to state whether it is their bona fide intention to be present at the meeting so that papers to be read for them by others or to be presented by title can be properly indicated on the program.

4—The committee recommends that the secretaries of the divisions and sections adhere strictly to the vote of the Council that no papers shall be presented at the meeting unless their titles appear in printed form on the final program.

The committee recommends that the Council discuss the desirability of extending the rule now in force in the Division of Industrial and Engineering Chemistry, with respect to abstracts, to all other divisions and sections of the Society. It has been suggested that all authors be required to submit a brief abstract of their paper to the Secretary of the division or section before which they wish to appear, supplying their abstract at the time their title is submitted for the program. In case of misplacements of papers the division or section secretary would forward abstract and title to the General Secretary who could then properly place the paper on the final program. It is recognized that under such a plan the closing date for papers on the given program would be a few days earlier than at present, but it is believed that the advantage to be gained would more than offset this slight disadvantage.

H. E. Howe, *Chairman*

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COMMITTEE ON GUARANTEED REAGENTS AND STANDARD APPARATUS

A note was published in the December number of the *Journal of Industrial and Engineering Chemistry* requesting members of the Society to inform the committee of specific instances of unsatisfactory deliveries of chemicals or apparatus. There was little response to this request for collaboration, but the committee has reason to believe from work done by its members and from correspondence with others that deliveries of unsatisfactory reagents and apparatus are frequently made. The committee has assisted some members of the Society to obtain satisfactory chemicals for certain purposes.

In discussions in regard to apparatus the committee hears many complaints about delay in the testing and certification of apparatus at the Bureau of Standards. This question was considered from various points of view. Members of the committee visited the Bureau, meeting the Director and observing the testing of some kinds of apparatus. The committee believes that steps have been taken which will improve the conditions governing this work. With the present tendency to decrease appropriations for the scientific work of the government departments and the difficulty in obtaining persons to do the work at the salaries which can be paid, the committee feels that this question is one on which the Society may well continue to coöperate with the Bureau of Standards.

The committee was invited to a conference with members of the Bureau of Standards who have been studying the question of suitable glass tubing for making lamp-blown apparatus. It was felt that the project was still at a stage where it could be handled best by the Bureau of Standards. The committee believes that the practical problem of securing a reliable uniform supply of such tubing is one which is of fundamental importance if we are to have wholly American-made apparatus. The question is an economic and business matter rather more than it is technical.

Work has begun on the obvious task of preparing specifications for reagents. Manufacturers have given full details of their specifications and tests for the three acids and ammonia which were taken up for consideration. A number of complete analyses have been furnished from different laboratories and results are available of tests covering six or eight years in one laboratory. The committee has data to show what has been delivered in the past on orders for these reagents. Complete specifications have not been drawn up by the committee for any of these reagents. It was felt that a report of tentative specifications presented merely for discussion at this time would have little value.

The multiplicity of sizes and shapes of the ordinary laboratory apparatus has been a cause for complaint from dealers, manufacturers, and users. The committee has gathered some data and made some tentative selections of sizes and shapes for some of the common articles. These selections have not yet been submitted to manufacturers, and it does not seem worth while to publish them before they have been considered by the manufacturers. The Association of Scientific Apparatus Makers of the United States has a committee on Standardization of Chemical Apparatus with which your committee has been coöperating.

It is believed that all the lines of work which have been discussed in this report might profitably be continued during the coming year.

W. D. Bigelow, *Chairman*

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COMMITTEE ON COÖPERATION BETWEEN UNIVERSITIES AND INDUSTRIES

It is the unanimous opinion of your committee that it is desirable that such students as can spend five years in their training should add a year of graduate study at the close of the work leading to the Bachelor's Degree, rather than continue a fifth year in work covered by a fixed curriculum. The training of such students in methods of research is considered more important than an increase in the number of formal courses of an undergraduate character. Some advanced courses should, however, be taken by such students during the fifth year. It is further the opinion of our committee that four years is too short a time for the thorough training of a professional chemist.

Professor Ellery has reported that an arrangement has been made by which advanced students in chemistry at Union College are permitted to attend the colloquia held by workers in the research laboratory of the General Electric Company. Such an arrangement is evidently very useful and it is hoped that the research laboratories of other companies may follow the example which has been set.

W. A. Noyes, *Chairman*

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REPORT OF THE COMMITTEE ON OCCUPATIONAL DISEASES IN THE CHEMICAL TRADES

Since the last annual report (Buffalo Meeting, April 1919) some matters of interest have been the concern of your Committee on Occupational Diseases in the Chemical Trades which promise to be of importance.

(1) EYE PROTECTION—A representative of the committee (Dr. R. B. Moore or Dr. C. L. Parsons) has attended all the conferences of the General Advisory Committee on Industrial Safety Codes held under the auspices of the Bureau of Standards at Washington. A plan of procedure, after discussions and much correspondence, has been agreed upon. Specifications for goggles for different purposes have been drawn up and discussed, and will soon be ready for issuance. The specifications may be had, on application, from the Bureau of Standards.

(2) INFLUENZA AND POISONOUS GASES—Data on the probable prophylactic action of very dilute chlorine against influenza have been collected and a summary of the facts published in the *Journal of Industrial and Engineering Chemistry*, **12** (1920), 293.

Immunity from influenza of workers in bromine plants is certainly indicated from the experiences in the largest producers in the United States. Just the contrary appears from data secured from smaller producers and users. It is to be hoped that an investigation of this matter may be undertaken.

In connection with this it may be mentioned that Dr. Louis I. Dublin, Statistician of the Metropolitan Life Insurance Company, has secured other interesting data on the immunity against influenza of people in illuminating gas works. Dr. A. Gregor[1] has found the number of cases of influenza among cordite and tin workers in fumes to be one-sixth to one-third of those not subject to fumes. Dr. F. Shufflebotham[2] found one-twenty-fifth to one-fifteenth the number of cases of influenza in poison gas factories. Dr. Gregor's further studies[3] indicate that the immunizing action of nitrogen dioxide and sulfur dioxide is due to the production of an acid medium in the upper respiratory passages which is inimical to microbial growth. An influenza outbreak was stamped out at a military camp by sulfur dioxide.

Mr. H. N. Jordan, Semet-Solvay Company, Syracuse, has found that a liberal and deep application of lanoline to the interior of the nose prevents the sensitive condition of the mucous membrane from irritating gases and germ infection which causes colds, etc.

(3) WOOD ALCOHOL—By invitation the chairman addressed the New York Academy of Medicine upon "Some Chemical Aspects of the Wood Alcohol Problem." The paper in full will appear in the *New York Medical Journal*. Certain phases of the subject are dealt with, especially some relative to prohibition, in a paper to be presented at the St. Louis meeting of our Society. The chairman has conferred with and assisted officials of the Society for the Prevention of Blindness. At least 90 per cent of the producers of refined methyl hydroxide have agreed

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[1] *Brit. Med. J.*, March 1 (1919), 242

[2] *Ibid.*, April 1919, 478.

[3] *Ibid.*, October 1919, 523.

to eliminate the word "alcohol" entirely from their labels, using "methanol" instead. Their advertisements now so read. It is to be hoped that every chemist will endeavor to render the designations "wood alcohol" and "methyl alcohol" obsolete.

No material changes in state laws have been made since 1912. This has been learned by correspondence with all the secretaries of the states. Administration of the present laws will conserve the public welfare and work little hardship upon the producers.

(4) DERMATITIS AMONG CHEMICAL WORKERS—Dr. E. R. Hayhurst, Ohio State Department of Health, reports to the committee numerous complaints of dermatitis by workers in rubber plants, seemingly due to the use of hexamethylenetetramine as an accelerator.

Dr. W. S. Landis has directed attention, in Bulletin No. 10 of the American Cyanamid Company, to the fact that "liquor and cyanamide are quite antagonistic." Heavy drinkers are unable to work in an atmosphere containing cyanamide. The dust seems to produce a skin irritation resembling eczema with those who imbibe mildly. This does not seem to have been the case in certain European plants, according to Dr. C. L. Parsons, and is now apparently of passing interest only in America.

A note published in the *Journal of Industrial and Engineering Chemistry*, 11 (1919), 797, on development of skin diseases in working with certain lubricants created not a little correspondence and did some good.

More publicity of an educational nature in regard to occupational rashes is deemed advisable.

(5) OCCUPATIONAL DISEASES AND DYE INDUSTRIES—Dr. T. H. Cone, National Aniline and Chemical Company, presented a valuable paper at the Eighth Annual Safety Congress, entitled, "Dangers in the Manufacture of Dyes." The risks "are largely centered about the manufacture of intermediates." The explosion risks are the greatest, the dyes themselves being the dangerous element. "Be extremely critical toward dyes which are to be handled in the form of dry powders, unless they are well supplied with sulfonic acid groups."

In connection with the above, particular attention is directed to a most valuable report by Dr. Alice Hamilton, entitled "Hygienic Control of the Anilin Dye Industry in Europe," which has been reviewed and commented on by the chairman of the committee in the April number of the *Journal of Industrial and Engineering Chemistry*.

(6) COÖPERATION WITH NATIONAL SAFETY COUNCIL—The National Safety Council has now nearly 4,000 members, including almost all the important industries doing safety work. The chairman continues his membership for the CHEMICAL SOCIETY as the National Safety Council has become a clearing house for safety experiences. While many of these are specifically accidental in character and might not appear to come within the scope of the activities of this committee, yet many are distinctively occupational and deal directly with prevention of diseases, acute and chronic, growing out of, or arising from, the chemical trades. The *National Safety News* has become a valuable medium for the dissemination of information on every phase of industrial development. The *Safety Practice Pamphlets* distributed to members are alone worth the annual dues. Attention of chemical manufacturers, not already familiar with this excellent agency, is especially directed to the National Safety Council by the committee.

(7) INSTITUTE FOR INDUSTRIAL HYGIENE—On November 14, 1919, a serious conference on Industrial Hygiene was held at the request and under the auspices of the Rockefeller Foundation at the Yale Club, New York City. Copies of the personnel list and digest of the important discussions may be had from Mr. E. R. Embree, Secretary of the Foundation, 61 Broadway. The contribution of your chairman, who was one of the guests, is given *in extenso*. This has later been published in the *Journal of Commerce* (New York, February 23, 1920) and will appear also in *Modern Medicine* (Chicago). The need of education and sane publicity, adequate social workers of qualified knowledge, and the necessity for research, with the coöperation of the chemist but the direction of a preventive medicine welfarer, were pointed out by your representative. The necessity for a program of magnitude calling for large financial support was agreed upon in principle, although there were the expected personal differences as to details by the experts present.

The trustees subsequently decided not to undertake the project, due to no lack of appreciation and sympathy, but for fear "that any studies or activities which in any way affected the industrial field would be subject to some prejudice and misunderstanding if carried on by one of the large foundations." General Schereschewsky advocated it as a Federal function, perhaps as a part of the United States Public Health Service. The subject is one of fundamental importance, not only because its purpose is humanitarian, but because it is good business to have workers healthy. Our SOCIETY should, and no doubt will, coöperate with other agencies in the furtherance of a project so commendable.

(8) FINANCIAL SUPPORT—It is patent to anyone giving the matter consideration that the work of our committee has not been systematic. Although something of distinct value has been accomplished in the way of research, in legislation, and in publicity, it could not be organized on a satisfactory basis for the very good reason that it has had no financial support. The time has arrived when the Council needs to give the matter serious consideration. We cannot get away from the responsibility.

The mephitic odor of the laboratory or the "works" covers a maze of mystery in the lay mind and is held responsible for numerous maladies. The word "chemical" is sinister. Where chemical processes are in operation, especially when fumes or vapors, even though the latter be only steam, are seen to escape from the works, there grows up a feeling of suspicion, often with reason, and all kinds of sickness are attributed to these "poisonous substances." If the chairman may judge from numerous letters and many conferences, even the members of the medical profession are not free from these sensations and confessions. And well they may be in many instances, for even though the action of many chemicals in varying degrees of concentration be known, the insidious effects of many more are absolutely closed books. They require most diligent study and painstaking research.

In this connection there is an urgent need for publication of an immense amount of valuable research carried on by the Chemical Warfare Service of the Army and Navy, which now appears to have little chance to reach the light of day. The data on the physiological factors and changes involved in fatigue are of immense value. The alterations in gas masks for use in chemical industries in peace-times constitute an important problem. A consideration of the few new facts collected bearing upon the seeming influence of certain toxic gases, referred to elsewhere in this report, opens a vista comparable to the hopeful days of the Pneumatic Institute, out of which came inhalation anesthesia, gaseous disinfection, and foundational knowledge of bacterial changes.

CHAS. BASKERVILLE, *Chairman*

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REPORT OF THE COMMITTEE TO FORMULATE SPECIFICATIONS FOR THE CONSTRUCTION OF A POLARISCOPE FOR LABORATORY USE

Before the committee was appointed there had been considerable correspondence among sugar chemists regarding the desiderata for a polariscope for ordinary laboratory use. The correspondents included the sugar chemists of the United States, Hawaii and Cuba and there were several conferences in the various places among the men who could arrange to meet. The correspondence regarding this matter was available to the committee and greatly facilitated our work. It has not been possible for our committee to arrange a meeting which all members could attend and most of our consultation has been by correspondence. There has been much personal conference among individual members of the committee however, and one conference was arranged at which five members of the committee were present. We have also had the advantage of the coöperation of manufacturers of optical instruments in this country, one of whom has made a polariscope during the last year which complies with the requirements of the committee.

GENERAL CONSTRUCTION

The general construction of the saccharimeter outlined in these specifications should be as simple and substantial as possible. All parts of the instrument should be easily accessible and the number of bolts and screws for holding the parts in place should be reduced to the necessary minimum.

So far as possible the instrument should have smooth, plain surfaces and be without unnecessary ornamentation. An irregular ornamented surface affords grooves and crevices for the accumulation of dirt and is not easily cleaned.

The instrument should meet the requirements of exposure to a humid tropical climate and must be constructed to withstand corrosion.

The construction of the saccharimeter, so far as possible, should be of such a type that repair parts can be furnished separately, thus obviating the expense, the delay, and the danger of shipping the entire instrument. Wherever this is not practicable manufacturers should undertake to make repairs in a satisfactory manner without undue delay.

HEIGHT

The standard height of most saccharimeters from table to center of field eyepiece is between 32 and 34 cm. This height is convenient for manipulation with the elbow of the operator resting upon the table and has found most general approval.

MOUNTING

The saccharimeter should be mounted upon a rigid trestle support and not upon a tripod. Instruments mounted upon tripods are unstable and easily turned out of alignment, the result being an error in the zero point.

The base of the trestle should be a solid piece of metal at least 2 cm. thick, the bottom edge of which can rest at all points upon the table. A base elevated above the table by supporting knobs or projections lacks rigidity and has the disadvantage of permitting cover glasses and other objects to escape underneath.

As many chemists prefer to fasten their instruments to the table, the base of the trestle should be provided with slots or screw holes to facilitate this.

LAMP SUPPORT

The lamp end of the trestle should be designed to accommodate a strong removable bracket for the convenience of those who may wish to use it as a lamp support, thereby keeping lamp and instrument always in undisturbed alignment.

The holder of the lamp must be placed at the proper focal distance and should be adjustable. Bracket and holder should be designed so as to prevent transmission of heat to the polarizer of the instrument.

For rooms of constant temperature the lamp should be in a separate room.

TROUGH

The trough, or tube holder, should be of solid metal, in one piece, and sufficiently thick to prevent denting or bending under ordinary conditions of usage. The diameter of the trough at the top should be about 3 cm. and should be adjusted exactly to fit the end pieces of the observation tubes. The cross-section of the trough should be semi-circular in shape. A wedge-shaped trough does not give the necessary support to inversion tubes or other tubes of unstable equilibrium.

The length of trough should be 42 cm. This length is necessary for the accommodation of the control tube which is used for verifying the accuracy of the scale. The short 20 cm. trough does not permit the use of the control tube and is also inadequate for the polarization of sweet waters and other dilute solutions.

The base of the trough should be supported to the frame of the trestle and there should be a 2 mm. space between its ends and the rest of the instrument. This clearance allows the escape of any liquid which may be spilled in the trough and protects against warping of the trough and transmission of heat to the optical parts when polarizations are made at high temperature. The base of the trough must be parallel with the optical axis of the instrument.

The trough should be made removable for the accommodation of other forms of tube supports or baths that may be needed in special cases. Owing to the corrosive action of solutions, which may be spilled inside of the trough, the screws for fastening the trough should be on the outside.

TROUGH COVER

The trough should be provided with a hinged cover for excluding light. The cover should be long enough to cover the 2 mm. space between trough and splash-glass holders, and should fold back to a horizontal position where it can be used in case of need as a receptacle for tubes.

The hinges of the cover should not be riveted. Many chemists find the trough cover an encumbrance, and for the convenience of such it should be easily removable.

For the convenience of those who use continuous, or side-filled, polarization tubes, a slotted cover should be provided as an optional accessory.

SPLASH GLASSES

The splash glasses at the ends of the trough, for protecting prisms and wedges against dust and drops of liquid, should be mounted in holders which can be quickly removed, cleaned, and replaced without the use of tools. Slip holders with a tension spring are most generally preferred, and they should be designed to prevent sticking.

The two holders should be as near alike as possible, at least 1.5 cm. deep and so constructed that glasses can easily be removed for cleaning. For ease of replacement when damaged, the splash glasses should be of the same size as the standard polariscope tube cover-glass.

QUARTZ WEDGES

For a commercial saccharimeter all chemists prefer the compensating single-wedge system. The wedge should be of sufficient length to give a range of scale from —35 to 115 sugar degrees.

If quartz of sufficient optical purity to give this lower range cannot be secured, a dextro quartz plate should be provided as an accessory for use in invert polarization.

The driving mechanism of the wedge should consist of a vertical rod supported to the front of the trestle frame and provided at the bottom with a milled head about 7 cm. from the table and convenient for operation with either hand.

The spiral rack and pinion with which the driving rod connects should operate smoothly and without lost motion.

SCALE

The scale should be etched upon ground glass and read by transmitted light obtained from the light source of the instrument. The design of the instrument should be such that the scale can be illuminated, when continuous or control tubes are in upright position in the trough. The range of scale should be from —35 to 115. This upper limit is necessary for those who wish to determine purities without diluting below 20° Brix.

The scale should have an adjustable double vernier, for plus and minus degrees, and should easily be read to 0.05° to which end the magnifying power of the reading microscope should be amply large. The error of scale graduation should nowhere exceed 0.05°.

The adjusting screw for moving the vernier to the zero point of the scale should operate positively in either direction. In some instruments a spring is designed to act when the adjusting screw is withdrawn. The objection to such a spring is its liability to stick and not to operate as intended.

Before shipment, the scale of each instrument should be carefully standardized at suitable intervals throughout its entire range and the standardization values should be incorporated permanently in some way upon a plate attached to the instrument.

PROTECTION CASE

Scale and wedges should be enclosed in a tight protection case to prevent deposition of dust or spattering with drops of liquid. The covering of the case should be easy to take off, when it is desired to gain access to scale or wedge, by the removal of a few fairly large-size screws. The rim of the protection case should have a covered aperture for inserting the key of the adjusting screw.

Whenever desired the front of the case should be provided with a small thermometer having a range of 10° to 40° C. and with its bulb near the quartz wedge. The thermometer should be arranged so that it can be read in a darkened compartment by light obtained from the lamp which illuminates the instrument.

SCREEN

The protection case should be designed to accommodate a removable screen to protect the eye which is not in use from the glare of the lamp. The screen should have a diameter of about 15 cm. at the level of the two oculars.

ANALYZER

While the analyzer is one of the parts which should require least attention, there are occasions when it needs to be adjusted. It should be made fairly accessible and be provided with simple means for firmly securing the adjustment.

LIGHT FILTER

The light filter should be placed between the polarizer and light source of the instrument and should be so supported that it can be quickly thrown into the field or out without disturbing the position of the instrument.

The standard bichromate cell should consist of a glass tube 3 cm. long encased in a metal jacket with threaded ends to accommodate the screw caps for holding the glasses. The cell should have a sufficient diameter so as not to require refilling because of air bubbles during an ordinary campaign (or more than twice a year).

Many chemists desire a lightly ground glass over the aperture at the lamp end of the instrument to equalize the light. Such a glass, if properly tinted, might serve the double purpose of light filter and equalizer. As a matter of convenience the instrument should be equipped with a light filter consisting of a glass plate of the same depth of color and absorptive power as the standard light filter.

OCULARS

The oculars in front of the instrument for reading field and scale should focus with a screw motion. The sliding eyepiece is objectionable, owing to the ease with which it is pushed out of adjustment by the face of the observer.

The distance from center of field eyepiece to center of scale eyepiece varies in present instruments from about 3 to 6 cm. For convenience and rapidity in reading, the interval between the two eyepieces should lie within these limits.

FIELD

American chemists with few exceptions prefer the customary double field with vertical semi-circular halves. The field should be of good size, sharply defined, and not obscured with the rim or halo of extraneous light, which results from improper optical construction.

POLARIZER

The preferences as to polarizer are divided between the Lippich and Jellet-Cornu prisms. Many chemists, while admitting certain advantages of the Lippich polarizer, complain of its frequent disintegration along the sharp edge of the half-prism upon which the telescope is focussed, the result being an imperfect or shattered field. The disruption of the half-prism may result from a jar of the instrument or it may take place from no apparent cause. More saccharimeters are made unserviceable for this reason than for any other. The difficulty of repairing the damage, owing to the extreme fragility of the parts, renders the Lippich polarizer less suited for localities which are far distant from repair shops. Many chemists, on the other hand, who admit the greater stability of a modified Jellet-Cornu prism, complain of its lower degrees of sensitiveness owing to the pronounced dividing line of the field, the result either of too thick a film of balsam between the halves of the upper part of the prism or of imperfect alignment of the polarizer. The defects peculiar to each type of prism can largely be overcome by careful manufacture. There are many stable Lippich polarizers and many Jellet-Cornu prisms that are satisfactory in sensibility.

If manufacturers can make repairs rapidly and can furnish extra interchangeable half-prisms of easy adjustment, the usefulness of the Lippich polarizer would be much widened and the majority of chemists in fairly accessible localities would probably then prefer it. For remote tropical countries where repairs are difficult and time-consuming a modification of the Jellet-Cornu prism would probably be the better type. For these reasons the type of polarizer should in great measure be left optional with the purchaser. In their manufacture of polarizing prisms manufacturers should take every precaution to insure stability and to prevent drying out and cracking of the films of balsam cement.

A very serious complaint from tropical countries is the infection of the polarizer, analyzer, and other optical parts of the instrument by molds, the mycelia of which grow over the prisms, corroding their surface and obscuring the field. Efforts to prevent infection by enclosing the parts more adequately have not proved successful. The best means of preventing the growth of molds seems to be a construction that permits of easy accessibility and removal of parts for cleaning and for placing in desiccators during periods when the saccharimeter is not used.

MOUNTING OF PRISMS—Wax, as a mounting material for prisms, has proved objectionable in warm climates on account of its softening. A mounting in cork and plaster is said to be the most satisfactory.

HALF-SHADOW ANGLE—The fixed half-shadow angle of the polarizer in most saccharimeters varies from 5 to 9 angular degrees, the choice of angle by different manufacturers seeming to depend somewhat upon the length and pitch of the quartz wedge. It is probable that for general commercial purposes the half-shadow angle should fall within this range. The sensibility is greater but the intensity at the end-point is less with the smaller half-shadow angle. Recent improvements in electric stereopticon lamps with concentrated filament and high candle power make it possible for manufacturers to adapt saccharimeters to a lower half-shadow angle than was formerly the case. For a normal weight of 26 grams the fixed half-shadow angle should have a magnitude of at least 7° for the average class of sugar factory raw products. The angle may be smaller than this for colorless products. The angle may also be reduced for raw products with instruments which are adapted to a normal weight of 20 or 16.29 grams.

Chemists who work constantly with dark-colored sirups and molasses prefer a polarizer with a rather wide half-shadow angle. It would, therefore, be a distinct advantage if manufacturers could supply interchangeable polarizing prisms—one with a medium half-shadow angle between 5 and 8 angular degrees and another with a higher half-shadow angle between 9 and 12 degrees.

Polarizing prisms should be mounted in metal holders which can be easily removed and inserted and the adjustment of which can be quickly and securely fixed.

The sleeve, or cover, which protects the polarizer should be easy to take off by the removal of a few fairly large-sized screws.

The standard temperature for the calibration of saccharimeters shall be 20° C. For laboratories working at a temperature materially different from this, correction of polarizations to 20° C. may be made at discretion by any of the following methods:

1—By the use of a table of temperature corrections for each particular product.

2—By changing the normal weight.

3—By changing the capacity of normal flask.

4—By changing length of normal tubes.

5—By having a scale calibrated by the manufacturer so that it is correct for the temperature desired.

With the exception of the first method these methods of correction are strictly applicable only to products which contain no other optically active constituent than sucrose. For general sugar house and food products containing several sugars, in case constant temperature polarization at 20° C. is not permissible, Method 1 gives results which are nearest to those obtained at the standard temperature.

STANDARD OR NORMAL WEIGHT

A large majority of chemists believe that the present is a most suitable time to abandon the inaccuracies and inconveniences of previous national standards and to agree upon a saccharimetric scale which shall be accurate, convenient, and so far as possible international. From opinions expressed by leading chemists in America, England and France, it is apparently more easy to secure general agreement, in these three countries at least, upon the so-called international normal weight of 20 grams proposed in 1896 by Sidersky and Pellet. According to this standard the 100 degree point of the saccharimeter scale shall indicate the polarization of 20 grams of chemically pure dry sucrose dissolved in distilled water to 100 metric cc. and polarized in a 20 cm. tube, the temperature of solution and instrument to be 20° C. and the illumination to be white light filtered through a solution of potassium bichromate of such concentration that the percentage content of the solution multiplied by the length of the layer of solution in centimeters is equal to nine.

While many chemists believe that all saccharimeters hereafter manufactured for American use should be graduated solely according to this proposed international standard, it is the opinion of this committee that pending international agreement upon the question manufacturers of saccharimeters should standardize their instruments according to the scale desired by the individual purchaser.

In the adoption of an international saccharimetric standard this committee believes that—in order to avoid the numerous unfortunate changes which in the past have characterized previous standards, and in order to have absolute accuracy and uniformity in different parts of the world—the percentage content, specific gravity, refractive index and angular rotation of the normal sugar solution, and the angular rotation, in terms of sodium and mercury monochromatic light, of the quartz plate, which shall read 100 upon the saccharimeter scale, should be established by carefully conducted experiments in the governmental laboratories of the different countries; and that from the results thus found international agreement shall be reached in regard to the final values, upon which manufacturers shall base the standardization of their instruments. The U. S. Bureau of Standards has already completed investigations upon the rotation values and other constants of the 26 and 20 gram normal sugar solutions.

It is not intended that the establishment of an international normal weight shall throw out of use the large number of saccharimeters which are at present doing excellent service. The transition is to take place gradually as in the change from Mohr to metric cc. Old instruments as they wear out are to be replaced by instruments with the new scale. Owners can also have their old instruments rescaled but this should be done only when the accommodation of scale, polarizer, lenses, etc., secures an equal or greater accuracy in reading. If an old instrument is not rescaled it should at least be standardized and the weight of pure sucrose necessary to read 100 upon its scale be engraved or stamped upon a plate attached to the instrument. Correction of instruments by the adjustment of an incorrect scale to a correctly standardized quartz plate is open to criticism, as a scale thus adjusted is accurate only for the reading of the plate and a considerable error may be introduced at other points of the scale, especially when readings have to be corrected for dilution.

W. D. BIGELOW, *Chairman*

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REPORT OF THE COMMITTEE ON ENDOWMENT OF THE AMERICAN CHEMICAL SOCIETY

The committee, I. K. Phelps, *Chairman*, submitted a report which, in abstract, was as follows:

There is every reason why the AMERICAN CHEMICAL SOCIETY should be endowed since it shares with the universities the common purpose of the advancement of learning.

The endowment should be general rather than specific, for the SOCIETY is a living thing with changing needs. For instance, just now it may seem desirable to provide for improvements and extensions in *Chemical Abstracts*, but in the course of time the plan may be revived, which Ernest Solvay developed before the war, of an abstract journal in various languages to care generally for the chemists of the world. If this plan should ever be carried out, it might involve a duplication of effort to continue a line of work here which to-day is greatly needed.

SUGGESTED USES FOR ENDOWMENT

Conditions are now favorable for American journals to assume the leadership formerly held by German journals. The SOCIETY publishes three journals, all ably edited; but if the budget could allow adequate appropriations for the *Journal of the American Chemical Society* and *Chemical Abstracts*, and permit the *Journal of Industrial and Engineering Chemistry* to profit by its own earnings, all could be brought up to a better standard.

We have also to face the problem of publishing monographs and compendia. The urgency for the compilation and publication of these is extreme, but the funds are lacking.

If the Secretary's office could act as a clearing house for chemical information, coördinated with the National Research Council and the government activities, it could accomplish much in collating and spreading reliable chemical information. A traveling assistant secretary, as suggested by Mr. Little, could be added to that office with much profit.

Under present conditions, it will probably become necessary to raise the dues of the SOCIETY before long, thus cutting off from its benefits chiefly students and young chemists in the formative period. Such an increase in cost would, therefore, be a tax on progress.

While the more immediate purpose of the endowment is for the spread of knowledge rather than for its initial achievement, it would be unfortunate to forbid the authorities of the SOCIETY to use its funds for research if the need should arise.

PROPOSED PLAN OF SECURING ENDOWMENT

It is proposed that the present Endowment Committee be discharged after the completion of the work upon the plans for securing endowment; that two new committees be appointed by the President; the one (hereafter to be referred to as the Endowment Collection Committee) to carry out such plans of collecting endowment as shall be approved, the other (hereafter to be referred to as the Endowment Finance Committee) to receive and invest such moneys as are collected for endowment. This latter committee should have a banker included in its numbers.

To start the project, it is suggested that the Advisory Committee select definite objects, upon which the Endowment Collection Committee can make a campaign; that the appeal of this committee be for a Permanent Endowment Fund, the income only of which shall be available for expenditure at any time and the objects for which this income shall be expended to be determined by the Advisory Committee, the Directors or a new committee constituted for the purpose; that at the present time an attempt be made to secure one million dollars for this fund; that the Endowment Collection Committee consist of a chairman, who shall be appointed by the President and empowered to associate with himself such other helpers as may be approved by the President.

The following plans for use of the Endowment Collection Committee are suggested:

1—Direct appeal for contributions, under the advice of the President, to the end the appeals may not be overdone.

2—Appeals for bequests of definite sums by will from chemists, from chemical manufacturers, and from others.

3—Appeals for the purchase of Endowment Life Membership, to cost such a sum as shall by its interest during the life of the member defray his dues to the SOCIETY and at his death be transferred to the General Endowment Fund together with any excess in income which may be derived from the Endowment Life Membership Fund. This fund should be under the same management and control as the General Endowment Fund, and entirely separate and distinct from the present Life Membership Fund.

ORIGINAL PAPERS

LOW TEMPERATURE DISTILLATION OF SUB-BITUMINOUS COAL

By H. K. Benson and R. E. Canfield

LABORATORY OF INDUSTRIAL CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON

Received December 29, 1919

The results obtained from the low temperature distillation of a non-commercial lignite coal[1] in the state of Washington appeared of sufficient value to warrant further investigation on a semi-commercial scale. Such work is now under way with somewhat different apparatus on another lignite coal. In connection with the mining of sub-bituminous coals it has frequently been found unprofitable to work certain veins on account of their high ash content or other unmerchantable properties. For instance, the Bagley vein at Coal Creek, Newcastle, Washington, is described as being "too dirty" for the production of a commercial fuel and although of sufficient size is not worked. It seemed of interest, therefore, to ascertain the suitability of this material for distillation purposes.

DESCRIPTION OF SAMPLE

The coal is black in color, but the streak is brown-black as the powder shades off to brown. It has a rather dull luster, is massive in texture, without joints, and has a conchoidal fracture. The proximate analysis is given in Table 1.

TABLE I—PROXIMATE ANALYSIS OF NEWCASTLE COAL (PER CENT)

	Laboratory Sample		Sample Reported U. S. Geol. Sur., *Bull.* 474	
	As Received	Air-Dry	As Received	Air-Dry
Moisture	12.1	5.8	7.1	5.9
Volatiles	36.8	39.4	37.8	38.1
Fixed Carbon	40.7	43.6	42.9	43.1
Ash	10.41	11.15	12.2	12.9
Sulfur	0.34	0.36	0.34	0.38
Nitrogen	1.37	1.47	2.44	2.61
B. t. u.	10410.0	11150.0	10410.0	11300.0

APPARATUS AND PROCEDURE

The methods of procedure and the apparatus were with a few minor modifications the same as previously described.

PRODUCTS OF DISTILLATION

The yield of raw products at the different distillation temperatures is given in Table 2.

TABLE 2—YIELD OF DISTILLATION PRODUCTS

Temperature ° C.	Total Distillate Per cent	Dry Tar Per cent	Aqueous Solution Per cent	Coke Per cent	Gas Cu. Ft. per Ton
150	6.9	...	6.9	90.2	3
200	9.2	0.5	8.7	85.1	8
250	17.1	1.9	15.2	74.1	22
300	18.3	2.8	15.5	70.6	2070
350	19.8	3.5	16.3	67.2	3540
400	18.9	3.2	15.7	66.1	4850
450	18.7	2.8	15.9	65.3	5990
500	17.7	2.3	15.4	64.2	6910
550	17.1	1.6	15.5	63.1	7670
600	16.1	1.0	15.1	62.2	8310

GAS

A wet test meter was used for measuring the gas the yields being indicated in Fig. I. The gas samples were analyzed in a Morehead gas apparatus and the percentage composition is given in Table 3.

TABLE 3—PERCENTAGE COMPOSITION OF GASES

° C.	CO_2	Ill.	O_2	CO	H_2	CH_4	N_2
250	45.1	3.3	1.4	7.1	0.3	8.6	34.2
300	33.2	3.8	0.8	8.3	0.9	10.7	42.3
350	20.4	4.9	0.4	9.6	8.1	23.6	33.0
400	18.9	5.0	0.4	11.8	9.8	21.2	32.9
450	17.3	4.9	0.4	13.3	11.5	20.2	32.4
500	16.4	5.1	0.4	14.5	13.0	18 4	32.2
550	14.1	5.1	0.4	15.6	15.1	17.8	31.
600	12.6	5.3	0.4	16.8	15.9	17.2	31.8

The calorific values calculated by Lunge's method are plotted against the temperatures of distillation in Fig. II.

COKE RESIDUE

The coke obtained up to 500° C. was of a dull black color and retained more or less the size and form of the original particles. From this point to 600° C. the particles possessed more of a metallic or silvery luster and swelled slightly in size. Its composition is given in Table 4, which also shows the yields per ton of coal. In Fig. III is shown the increase in calorific value with increase of temperature. The thermal values of the coke were obtained by means of the Emerson bomb calorimeter.

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[1] THIS JOURNAL, 9 (1917), 946.

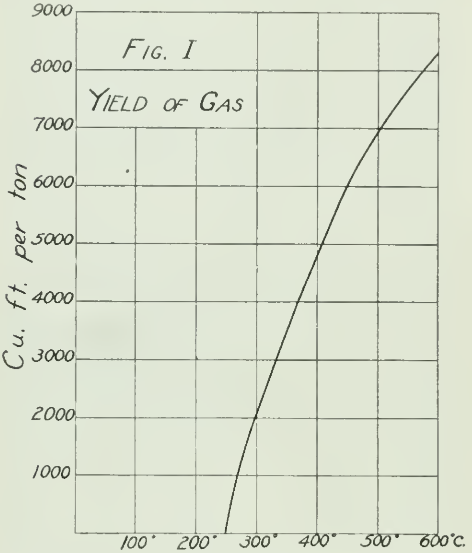
FIG. I
YIELD OF GAS

TABLE 4—YIELD AND COMPOSITION OF COKE

Temp. °C.	Coke Lbs.	Volatiles Per cent	Ash Per cent	Nitrogen Per cent	B. t. u.
150	1804	38.0	14.3	2.9	11,800
200	1702	31.8	15.1	2.7	12,210
250	1482	26.7	17.5	2.5	12,500
300	1412	22.5	18.2	1.8	12,690
350	1344	19.4	19.3	1.4	12,790
400	1322	16.2	19.5	1.1	12,870
450	1306	13.1	19.9	0.9	12,930
500	1284	9.9	20.1	0.7	12,980
550	1262	6.8	20.4	0.6	13,020
600	1244	4.1	20.7	0.5	13,040

AMMONIACAL LIQUOR AND CYANIDES

The total distillate was well washed and the washings tested for ammonia and cyanides. Most of the ammonia was found to be held by the tar before it reached the acid wash bottle, while the cyanogen content seemed to be nearly all carried over to its respective wash bottle. The cyanide precipitated out upon the addition of ferric alum even at the lower temperatures. As this precipitate was intermixed with impurities, as noted by the color, no significance would attach to the amounts obtained at the various temperatures, but it was estimated that approximately 1.25 lbs. of cyanogen may be obtained at 600° C. per ton of coal. The yield of ammonium sulfate in pounds per ton of coal is given in Fig. IV.

TAR OILS

All of the water was extracted by calcium chloride from the crude distillate and the dry tar obtained was red-brown in color and semi-solid at ordinary temperatures. Its specific gravity ranged from 0.975 to 1.033. The oils were distilled in small glass retorts and the percentage yields are given in Table 5, including the hard and soft paraffin separated by a modification[1] of Eisenlohr's method.[2] About half a gram of the paraffin oil was weighed to the nearest milligram in a tared 7-in. test-tube and warmed slightly.

TABLE 5—PERCENTAGE COMPOSITION OF OILS

Temp ° C.	To 150° C. Light Oil	150°–300° C. Medium Oil	Above 300° C. Paraffin Oil	Hard Paraffin	Soft Paraffin	Coke	Loss
250	10.3	42.1	33.1	3.9	1.3	9.6	4.3
300	10.7	42.5	33.4	5.0	1.8	10.0	3.3
350	11.3	41.9	33.9	5.5	2.1	9.7	3.2
400	10.5	41.7	33.2	5.2	1.9	10.3	4.3
450	9.3	41.4	31.4	3.4	1.5	13.6	4.3
500	7.8	41.5	39.8	2.1	1.4	15.9	5.0
550	5.9	41.2	29.2	0.9	0.7	17.6	5.9
600	3.9	40.9	27.8	0.6	0.5	21.1	6.3

TABLE 6—YIELD OF OILS IN POUNDS PER TON OF COAL

Temp. ° C.	Raw Tar	Light Oil	Medium Oil	Paraffin Oil	Hard Paraffin	Soft Paraffin
250	38	3.9	16.0	12.6	1.5	0.5
300	56	6.0	23.8	18.7	2.8	1.0
350	70	7.9	29.3	23.7	3.8	1.5
400	64	6.7	26.7	21.2	3.3	1.2
450	56	5.2	23.2	17.6	1.9	0.8
500	46	3.6	19.1	13.7	1.0	0.6
550	32	1.9	13.2	9.3	0.3	0.2
600	20	0.8	8.2	5.6	0.1	0.1

Twenty cc. each of ethyl ether and ethyl alcohol were added and the mixture cooled to —20° C. in a salt and ice bath. The flaky mass was filtered through a 4-in. funnel surrounded by freezing mixture, the filtrate being evaporated and the soft paraffin determined by freezing from an ether-alcohol (1 : 2) mixture after evaporating upon the water bath. Any admixture of impurities was removed by dissolving the paraffin in the filter by pouring boiling ethyl alcohol through it and collecting the filtrate in a tared beaker, the alcohol evaporated and the hard paraffin (m. p. 45° to 55° C.) weighed.

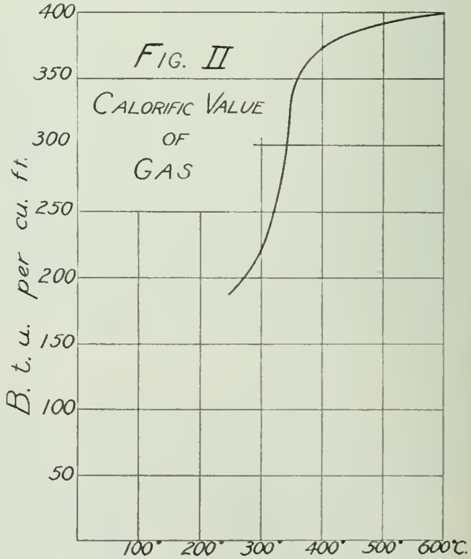
FIG. II
CALORIFIC VALUE OF GAS

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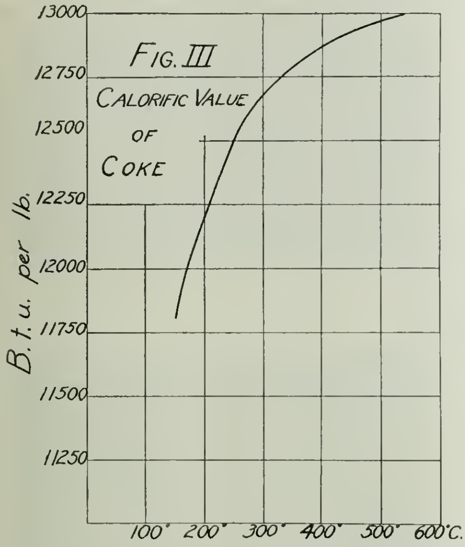
[1] School of Mines and Metallurgy, Univ. of Missouri, *Bulletin* [4], 3, 55.

[2] *Z. angew. Chem.*, **1897**, 300, 332.

PROPERTIES OF TAR OILS

The light oils were washed with sodium hydroxide and sulfuric acid, 20 per cent being soluble in alkali.



The washed oils were then treated with concentrated nitric and sulfuric acids in a reflux condenser, whereupon nitro derivatives were obtained to some extent, but the limited amount of oils obtained made it impractical to ascertain the yield. Phenols also were isolated upon the addition of bromine water to the cresols obtained from the alkali washings. The specific gravities of the various fractions are recorded in Table 7.

TABLE 7—SPECIFIC GRAVITY OF TAR FRACTIONS

Temp. ° C.	Light Oil	Medium Oil	Paraffin Oil
250	0.807	0.905	0.939
300	0.815	0.908	0.950
350	0.812	0.915	0.957
400	0.815	0.926	0.968
450	0.816	0.935	0.966
500	0.816	0.938	0.978
550	0.818	0.946	0.983
600	0.821	0.955	0.985

DISCUSSION

The most striking feature of the investigation is the well-defined decomposition point between 350° C. and 400° C., approximating closely the same temperature as in the previous study, *viz.*, 380° C. This marks a maximum in the yield of tar oils, and an abrupt rise in the quantities of hydrogen and methane, the change of composition in the gas being evident from the shape of the curve (Fig. II). At this point also occurs a decrease in paraffins, suggesting the possibility of the cracking of the oils.

Unlike the previous study, the presence of cyclic compounds in the light oil was proved by the formation of nitro derivatives and phenols. The light oils were distilled[1] and very small amounts of benzene (to 95° C.) and toluene (95° to 120° C.), and a considerable amount of solvent naphtha (120° to 200° C.) were recovered. The light oils soluble in sodium hydroxide constitute the cresols and unsaturated acids. The medium oil is made up in part of naphthalene, anthracene, and the higher paraffins, and is semi-solid at ordinary temperatures. Soft pitch is contained only in tars obtained at 500° C. and above.

CONCLUSIONS

I—The maximum yield of tar oils is obtained at 350° C.

II—About 3.5 per cent of the coal may be obtained as raw oils.

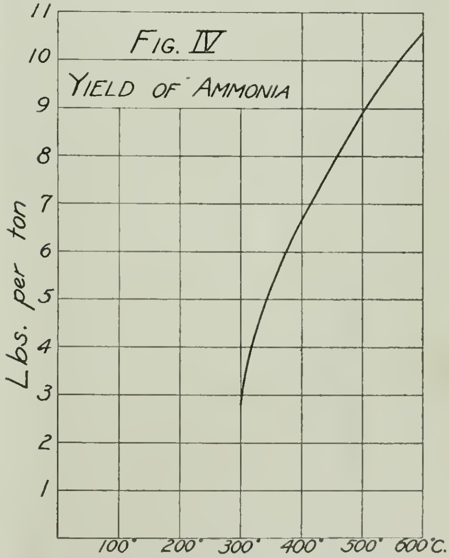
III—These raw oils are a mixture of coal tar and petroleum-like oil, with the former predominating.

IV—The yield of light oils decreases rapidly as the temperature increases, that of the paraffin oils less rapidly, while the yield of the medium oils remains fairly constant.

V—About 5.3 lbs. of paraffin wax per ton of coal may be obtained at 350° C.

VI—The gas given off up to 600° C. is small in volume and low in heat value, but relatively high in illuminants.

VII—Appreciable amounts of ammonia may be obtained from the tar water and also small amounts of cyanides.



VIII—The specific gravities of the tar oils and their respective fractions increase correspondingly with increase in the temperature of distillation.

IX—This coal, when subjected to destructive distillation, has a temperature of marked decomposition which corresponds to a sudden increase in the amounts of hydrogen and methane evolved and a corresponding increase in the quantity of oil distilled which is generally the maximum point, and, as in most low-grade coal, this temperature lies between 350° and 450° C.

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[1] *Met. & Chem. Eng.*, **17** (1917), 551.

X—The residue at 350° has a calorific value of 12,790 B. t. u., which is an increase of 22.8 per cent over the coal as mined, and of 14.7 per cent over the dry coal.

HARDENING EFFECTS OF VARIOUS ELEMENTS UPON LEAD

By Carl O. Thieme

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Received November 22, 1919

During the war, the high price and the threatened famine in tin, due to labor conditions, shortage of ship bottoms, and possibly to the submarine warfare, caused the manufacturers of this country to search and experiment with other metals and alloys that could be used in place of those containing tin. Of course, the greater portion of this work was done on tin-base bearing metals, but the conservation of tin was aided by the substitution of other metal for tin, in brass and bronze alloys.

It is quite well known that the composition of gun metal, 88-10-0-2, was modified to 88-8-0-4, with results that were just as satisfactory. In other cases, tin was entirely omitted from bronzes, and aluminum substituted, producing alloys that were decidedly superior to the tin bronze, with regard to physical properties, although as a general rule difficulty was encountered in manufacturing aluminum bronze castings. Commercial manganese bronze, which is essentially a copper-zinc-iron alloy, found a greater use, and the use of yellow brass mixtures in general became more popular. The tin content of brass mixtures containing the four elements, copper, tin, lead and zinc, in many instances was decreased, and one or two of the other metals increased, producing alloys that were cheaper and gave just as satisfactory results for the purposes for which they were used.

Hardening Effect of Various Elements on Lead

Composition (Per cent)											Hardness			
Cu	Sn	Pb	Sb	P	Mg	Ca	Na	Ni	As	Hg	Magnified Hammer Scleroscope	Brinell Test	Fig. No.	Remarks
...	..	99.0	..	..	...	0.8-1.0	...	...	...	...	14.0	15.0	...	An admixture of barium and calcium, sometimes added as hardening agent
...	..	99.5	..	..	...	...	0.5	...	...	...	...	5-6*	...	
...	..	99.2	..	..	...	...	0.8	...	...	...	...	7.5-8*	...	
...	..	99.5	..	..	...	...	...	...	0.5	...	...	7.5-8.5*	...	Known as shot lead. also added to antimonial lead for bullets
...	..	98.0	..	..	...	...	...	2.0	...	...	...	....	...	Hardness not determined
...	..	90.0	10.0	..	...	...	...	...	...	...	10-11	14.0	1	Popularly known as antimonial lead
...	..	82.0	18.0	..	...	...	...	...	...	...	14.0	16.0	2	Metallic packings—filling and hammer metal
0.8	Trace	81.0	18.0	0.15	...	...	...	...	...	...	...	24.0	3	
...	..	82.0	17.5	..	0.5	...	...	...	...	...	...	17.5	...	Experimental alloy
...	0.5	82.0	17.5	..	...	...	...	...	...	...	...	15.5	...	
...	4.0	82.0	14.0	..	...	...	...	...	...	...	10-12	18.0	4	
...	5.0	81.0	14.0	..	...	...	...	...	...	...	11-13	19.0	...	
...	8.0	80.0	12.0	..	...	...	...	...	...	...	14-15	20-21	5	
...	11.0	75.0	14.0	..	...	...	...	...	...	...	15-16	22.0	6	
...	..	99.3	..	..	0.7	...	...	...	...	...	12.0	15.0	7	Experimental alloy
...	1.0	98.3	..	..	0.7	...	...	...	...	...	...	12.0	...	Experimental alloy
...	2.5	96.8	..	..	0.7	...	...	...	...	...	...	10.5	...	Experimental alloy
...	5.0	94.3	..	..	0.7	...	...	...	...	...	...	12 0	...	Experimental alloy
...	..	...	..	..	...	...	...	...	...	0-7.0	...	4-9*	...	
...	..	100.0	..	..	...	...	...	...	...	...	...	4-4.5*	...	Cast lead
...	..	100.0	..	..	...	...	...	...	...	...	...	5-5.5*	...	Cold hammered lead

* Hardness numbers followed by asterisk. 100 kilogram load and 10 mm. ball; all others, 500 kilogram load and 10 mm. ball.

As stated above, the conservation of tin was due largely to the use of lead-base and leaded white metals. It is not my intent to enter into a discussion of the values of lead-base bearing metals at this time, for there are many articles, pro and con, published on this subject, but to present the following data which will show the hardening effect of the various elements upon lead.

The hardening effect of the elements will be taken up in the order in which they appear in the accompanying table.

CALCIUM—Lead may be hardened by the addition of about one per cent of calcium.[1] It then has a Brinell hardness of 15, and quite a metallic ring. The alloy does not long retain a luster, and in a short time darkens a great deal. It shows numerous small blisters appearing on the surface of the metal, which will chip off, giving the metal a sort of pocked appearance. We believe that this alloy, upon remelting several times, loses its hardness, due, undoubtedly, to the oxidation and consequent skimming off of the calcium, together with the lead oxide. An admixture of barium and calcium is sometimes added as the hardening agent.

SODIUM—Sodium added to lead hardens it considerably, giving a Brinell hardness of approximately 5 to 6. This alloy also loses its hardness after several remelts. It is believed by some that the hardening constituent in an alloy of this kind is a substance having the formula Na_2Pb_5.[2] The eutectic of lead-sodium alloys is 2.5 per cent sodium, and 97.5 per cent lead. As the sodium is increased, the Brinell hardness gradually increases until at 0.8 per cent (the maximum amount of sodium dissolved by lead) the Brinell hardness is 8. From 0.8 to 2.5 per cent the hardness does not increase, but falls off with sodium values higher than 2.5 per cent.

ARSENIC—Arsenic hardens lead and increases the fusibility of the alloy. The quantity of arsenic added is generally under one per cent, and probably not more than 0.5 per cent. On account of the increased fusibility, this metal is used to advantage in making lead shot, for the time taken in solidifying gives the metal better opportunity to form a spherical drop.

NICKEL—Nickel, when added to lead, has a decided hardening effect, but on account of the great difference in their melting points, the use of this alloy is rather out of the question. The component metals must be melted separately, and mixed in the molten condition. An alloy of 2 per cent nickel and 98 per cent lead has a good appearance and is quite resonant.

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[1] *Chem. & Met. Eng.*, Sept. 28 (1918), p. 253.

[2] C. H. Desch, "Metallography," 2nd Ed., **1913**; C. H. Mathewson, *Z. anorg. Chem.*, **50** (1906), 171.

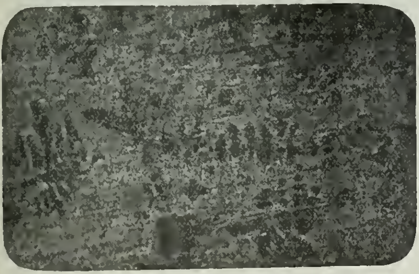

Fig. 1[1]—Matrix of Lead-Antimony Eutectic. Excess Lead Showing as Crystallites

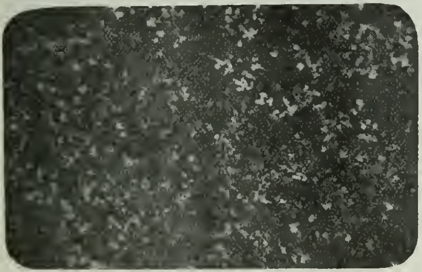

Fig. 2—Matrix of Lead-Antimony Eutectic. Excess Antimony Crystals Distributed Uniformly throughout the Section

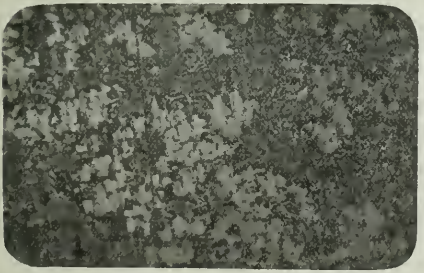

Fig. 3—Matrix of Lead-Antimony Eutectic. Free Antimony Crystals in Excess in Which Is Dissolved Compound Cu_2Sb

ANTIMONY—Antimony has long been used to harden lead, and has a wide use commercially as filling metal and hammer metal, and in some instances as an anti-friction metal. When the alloy contains more than 18 or 20 per cent antimony, it becomes too brittle for practical use. The hardness is proportional to the antimony content, and the increase is due to the formation of a eutectic having the composition 87 per cent lead and 13 per cent antimony. The hardness is increased approximately one number (Brinell) for each per cent of antimony added up to the eutectic point, when the proportionate increase of hardness in the alloy does not hold true. The hardness of a mixture of 10 per cent antimony and 90 per cent lead is approximately 14 Brinell, which corresponds to the calcium-lead alloy (Fig. 1).

An alloy of antimony and lead, of the composition 87 per cent lead and 13 per cent antimony, shows neither lead nor antimony in excess, and is entirely composed of the eutectic. When the antimony content is increased to 18 per cent the alloy shows a hardness of 16 Brinell. The grain of this metal, however, varies greatly and is controlled only with considerable difficulty by pouring into a water-cooled mold. In order to prevent segregation, it is necessary to pour this metal as near the melting point as possible. The mixture is quite resonant, and, unlike the calcium and the sodium hardened lead alloys, does not lose its hardness upon remelting. It is brittle and fractures easily. Fig. 2 shows structure of an alloy of the composition 82–18.

The addition of one per cent phosphor copper to the alloy just mentioned has a decided hardening effect, showing a Brinell hardness of 24.0. However, this alloy is more brittle than the antimony-lead mixture, and loses its luster more quickly. It is extremely hard to cast, as it pours very sluggishly, and segregation is bound to occur in spite of all precautions. This is explained by the fact that, in order to cast a sound bar, the temperature must be raised to increase the fluidity, and flotation of the antimony crystals results. The grain is finer than the 82–18 antimony-lead mixture, thereby offering an explanation for the increased hardness, and a fracture of the metal shows a finely crystalline grain, similar in color to gray iron. Fig. 3 illustrates the segregation of free antimony.

Magnesium hardens the alloy of antimony and lead, although not to as great extent as the addition of one per cent phosphor copper. One-half per cent of magnesium added to this alloy produces a metal having a hardness of 17.5. It is almost silvery white when first cast, but the luster slowly disappears and the alloy darkens.

One-half per cent of tin does not noticeably alter the properties of this alloy, although a series of hardness tests shows a slight decrease to 15.5 Brinell. A microscopical examination reveals the formation of a few imperfectly formed tin-antimony cubes, very unevenly distributed throughout the section. These crystals are absent in the other alloys. As the tin content is increased to 4 per cent, and the antimony decreased proportionately, the resultant alloy gives a Brinell hardness of 17.5 to 18.0 (Fig. 4). The addition of 5 per cent tin produces an alloy of 19.0 Brinell hardness. On increasing the tin content still further to 8 per cent, the structure of the metal is changed, and as the composition nears the hypothetical ternary tin-lead-antimony eutectic (none formed) we find a fine grained alloy. This is an ideal alloy of the three metals, due to the fact that it retains its luster better than the majority of lead-base metals of this series, and readily takes a high polish. Its hardness is 20.0 (Fig. 5).

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[1] All photomicrographs shown here are taken at 100 magnifications and are etched with a dilute solution of nitric acid in ethyl alcohol.

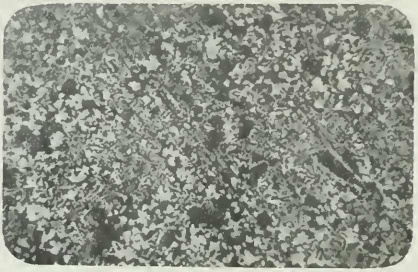

FIG 4—MATRIX OF LEAD-ANTIMONY EUTECTIC. IMPERFECTLY DEVELOPED TIN-ANTIMONY GAMMA CONSTITUENT AND A SMALL PERCENTAGE OF EXCESS LEAD

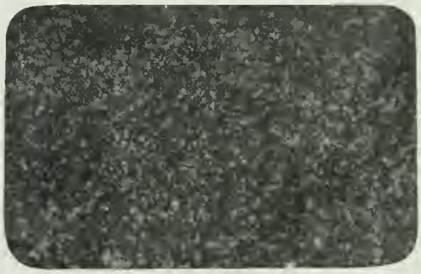

FIG. 5—LEAD-ANTIMONY EUTECTIC WITH A FLOTATION OF TIN-ANTIMONY GAMMA CONSTITUENT AND TIN CRYSTALS

An 11 per cent tin alloy of the same series gives a hardness of 21.5 to 22.0 Brinell (Fig. 6). It will be noticed in the tin-lead-antimony alloys that, as the tin is increased 1 per cent, the hardness is increased half a number in each instance. Most bearing metals of the lead-base series should not contain more than 10 per cent tin unless the antimony is increased proportionately. However, the alloy then becomes brittle, as in the case of the binary alloy of lead and antimony. Above 10 per cent tin, the addition of tin to lead-antimony alloys does not exert as great a hardening effect as is true when smaller percentages are added.

MAGNESIUM—Magnesium[1] hardens lead when added in small amounts, usually one per cent or under. An alloy containing one-half per cent magnesium has a Brinell hardness of 15.0. Difficulty is encountered, however, in alloying these metals. The alloys were made by introducing small pieces of magnesium into the molten lead until the former gradually melted and dissolved. After the magnesium is alloyed with the lead it does not oxidize rapidly, and, therefore, retains its luster and its hardness upon remelting. The writer believes the hardening constituent in this alloy to be a substance having the composition Mg_2Pb, which Kurnakoff and Stepanoff found to solidify at 551° C.[2] The photomicrograph (Fig. 7), although considerably scratched, illustrates the formation of this material.

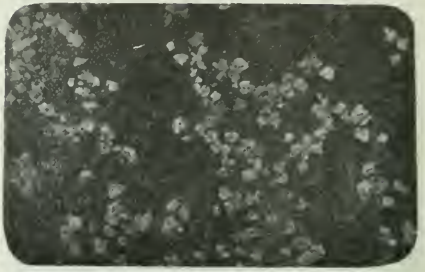

FIG. 6—LEAD-ANTIMONY EUTECTIC MATRIX IN WHICH IS IMBEDDED TIN ANTIMONY GAMMA CONSTITUENT

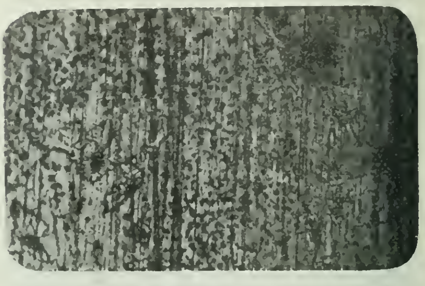

FIG. 7—MATRIX OF LEAD IN WHICH IS IMBEDDED Mg_2Pb CONSTITUENT AS PRIMARY CRYSTALLITES

The addition of one per cent tin to this mixture softens the alloy, giving a Brinell hardness of 12.0, while 2.5 per cent tin lowers it still further to 10.5. Between 2.5 and 5 per cent tin there is a limit to the falling hardness, and a mixture containing 5 per cent tin again raises the hardness to 12.0. An alloy of this composition would be rather expensive, as compared with the alloys previously mentioned, which give a greater hardness at a lower cost.

MERCURY—A recent investigation of lead alloys, with mercury, sodium, and tin, by J. Goebel,[1] shows that mercury, when added to lead, increases its hardness from 4 to 9 Brinell. Any amount of mercury up to a maximum of 7 per cent increases the hardness proportionately.

The hardness of cast lead and cold hammered lead is given at the foot of the table, to allow of comparison in degree of hardness.

THE SOLUBILITY OF MONO- AND DIAMMONIUM PHOSPHATE

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Received November 29, 1919

In connection with certain experimental work recently carried on in this laboratory, more definite information than could be found in the literature was required concerning the solubility of the two commercial phosphates of ammonia. It therefore became necessary to prepare solubility curves for these two salts which would be of sufficient precision for the work in hand. The temperature ranges in which we were interested were, for the mono-salt, from about zero to the boiling point of the saturated solution, and from 0° to about 70° C. for the di-salt. These solubility determinations were made with care, and with as great precision as was possible with the equipment in a technical laboratory. While we make no claims for the highest precision, we feel that the data are of sufficient value to warrant their general distribution.

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[1] *Metall u. Erz*, n. s., **7** (1919), 79; abstracted in *J. Inst. Metals*, **21** (1919), 435.

[2] Grube, *Z. anorg. Chem.*, **44** (1905), 117; **46** (1905), 177.

[1] *Z. Ver. deut. Ing.*, May 10, 1919; abstracted in THIS JOURNAL, **11** (119), 1065.

Dammer, Abegg, and the *Chemiker Kalendar* state that the di-salt, $(NH_4)_2HPO_4$, is soluble in four parts of cold water, and that the mono-salt, $(NH_4)H_2PO_4$, is less soluble than the di-salt. Comey adds that the mono-salt is soluble in 5 parts of cold water. Olsen[1] gives the same figure for the di-salt, but for the mono-salt he gives the solubility as 171 parts per hundred of water at 0° C. and 260 parts per hundred of water at 31° C.; that is, the mono-salt is much more soluble than the di-salt. The new edition of Seidell's "Solubilities" (1919) gives a value for the solubility of the di-salt, attributed to Greenish and Smith, of 131 g. $(NH_4)_2HPO_4$ in 100 g. water at 15° C.

THE SOLUBILITY OF MONOAMMONIUM PHOSPHATE, $(NH_4)H_2PO_4$

PREPARATION—The salt was prepared by recrystallization of commercial mono-salt, "Ammo-Phos," and analyzed as follows:

Per cent NH_3 = 14.80; Per cent P_2O_5 = 61.57; Ratio = 0.240.
Calculated for $(NH_4)H_2PO_4$:
Per cent NH_3 = 14.80; Per cent P_2O_5 = 61.72; Ratio = 0.240.

(By "Ratio" we mean the per cent ammonia divided by the per cent P_2O_5. For the mono-salt the "ratio" is 0.240, and for the di-salt 0.480.)

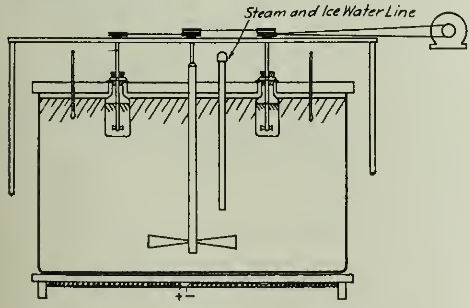

FIG. 1

METHOD—The apparatus used is shown diagrammatically in the accompanying sketch (Fig. 1). The temperature of the thermostatic bath was controlled by the introduction of steam or ice water, with an electrically heated hot plate as an auxiliary for the higher temperatures. For the very highest temperatures calcium chloride brine was used in the bath. This thermostatic bath was of large size and the water was kept in vigorous motion by a motor-driven propeller. Although hand controlled, no difficulty was experienced in maintaining the temperature constant to within 0.5° C., which was as precise regulation as was desired.

To each of two glass bottles of about 250 cc. capacity there were added water and an amount of the salt largely in excess of the requirement for a saturated solution at the temperature in question. One of these bottles was cooled to about 10° below the desired temperature, while the other was heated to about the same distance above it. The bottles were now placed in the bath, the agitators introduced, and vigorous agitation at constant temperature maintained for one hour. At the end of an hour the agitators were stopped and samples of the clear liquid withdrawn in the special weighing pipette shown in the sketch (Fig. 2), care being taken that the cotton filter on the end of the pipette was tight, preventing the introduction of crystals with the liquid. The agitators were again inserted and the stirring at constant temperature continued while the samples were being analyzed for ammonia by distillation. At the time of withdrawal of the sample a final temperature reading was taken in the bottles themselves by means of a carefully standardized thermometer. This temperature was considered the temperature of the determination.

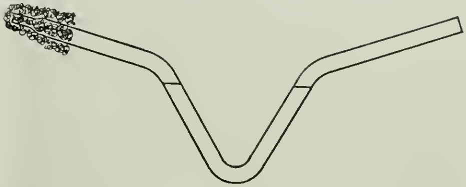

FIG. 2

If the two portions agreed sufficiently well, it was assumed that equilibrium had been reached; if they did not agree, two more samples were withdrawn. This was continued until satisfactory agreement was secured. This agreement was rarely obtained in less than 2 hrs.; almost invariably the bottle with the rising gradient reached equilibrium more rapidly than the bottle with the falling gradient. From the ammonia determinations, the amount of ammonium phosphate present in the sample, and hence the solubility, was obtained. This method of calculation is applicable, since the mono-salt is entirely stable at solution temperatures. An analysis of the material remaining in the bottles at the close of the series showed that the "ratio" had not changed at all during the experiments.

The method of procedure outlined was employed for all the determinations up to and including that made at 90° C. In the case of the measurement at 102° both bottles were brought to equilibrium from below. The last point, which is that of the boiling saturated solution, 110.5° C., was obtained by withdrawing the samples from a saturated solution during vigorous ebullition.

All thermometers used were checked by comparison with a standard thermometer. Where necessary, suitable stem exposure corrections were applied. We believe that the temperature measurements reported are certainly correct within ±0.5° C.

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[1] Van Nostrand's "Chemical Annual," 1918.

EXPERIMENTAL DATA—When the solubility data are calculated as percentage solubility, that is, as grams of salt dissolved in 100 g. of the saturated solution, and these results are plotted (Fig. 3), we find that the points up to and including 90° C. lie in a straight line, none of the determinations lying off the straight line by an amount greater than the experimental error. From this straight line we derive the equation for the solubility of the mono-salt over the temperature range of 5° to 90° C. as follows:

Solubility of Monoammonium Phosphate (g. in 100 g. of saturated solution between 5°–90°) = $18.0 + 0.455t$

The two high temperature points fall a little below the straight line, probably on account of the difficulty in withdrawing samples from the highly concentrated solutions. No determinations were made at temperatures below 5° C. but it is probable that the curve could be extrapolated at least to zero.

In Table I, which follows, are shown the experimental data and the solubilities derived therefrom. Column 1 shows the percentage solubility in the bottle which was heated to the required temperature, obtained by dividing the observed percentage of ammonia by 14.80 (the per cent of ammonia in monoammonium phosphate). Column 2 gives the percentage solubility in the bottle which was cooled to the desired temperature, and Column 3 gives the mean of Columns 1 and 2. Column 4 gives the percentage solubility as calculated by use of the above formula, and Column 5 gives the values of Column 4 recalculated as grams salt dissolved in 100 g. water.

TABLE I—SOLUBILITY OF MONOAMMONIUM PHOSPHATE, $(NH_4)H_2PO_4$

	Grams Monoammonium Phosphate				
	100 G. of Saturated Solution				100 G Water
Temp. ° C.	(1)	(2)	(3)	(4)	(5)
4.8	20.5	20.3	20.4	20.2	25.3
18.3	25.9	26.6	26.3	26.3	35.7
30.0	31.4	31.7	31.6	31.7	46.4
40.0	36.1	36.3	36.2	36.2	56.7
50.0	40.8	40.8	40.8	40.8	69.1
69.0	49.7	49.8	49.8	49.4	97.7
90.0	59.3	58.8	59.1	58.9	143.0
102.0	63.2	..	63.2	64.4	181.0
110.5	67.3	..	67.3	68.3	215.0

THE SOLUBILITY OF DIAMMONIUM PHOSPHATE, $(NH_4)_2HPO_4$

PREPARATION—The diammonium phosphate used in these experiments was prepared by ammoniating at a temperature above 80° C. a nearly saturated solution of mono-salt, cooling the mixture and filtering out the di-salt crystals. The air-dried crystals analyzed as follows:

Per cent NH_3 = 25.8; Per cent P_2O_5 = 53.9; Ratio = 0.479

Calculated for $(NH_4)_2HPO_4$:

Per cent NH_3 = 25.8; Per cent P_2O_5 = 53.8; Ratio = 0.480

METHOD—While the mono-salt is very stable at solution temperatures, the di-salt is much hydrolyzed, and precautions have to be taken, particularly at higher temperatures, to minimize ammonia losses. In the apparatus used by us it was not possible to entirely eliminate this loss, but its amount was determined in each experiment and its effect on the results as a whole largely eliminated by proper weighting of the experimental results.

The experimental procedure was practically the same as that used for the mono-salt, except that two samples were withdrawn from each bottle instead of one, as formerly. One sample from each bottle was analyzed for ammonia, and, if these showed satisfactory agreement, the other pair were analyzed for P_2O_5 by precipitation of the double magnesium salt. From the two analyses it was possible to arrive at the amount of decomposition which had taken place.

EXPERIMENTAL DATA—Table II gives the experimental data. The column headings are all self-explanatory, except possibly the last, which is intended to show the per cent of the dissolved phosphates of ammonia which was present as di-salt, as calculated from the "mean ratio." This column is of value in furnishing information as to the weighting of the data in deriving the solubility formula.

TABLE II—THE SOLUBILITY OF DIAMMONIUM PHOSPHATE $(NH_4)_2HPO_4$

Temp. ° C.	Per cent NH_3 Up	Per cent NH_3 Down	Per cent NH_3 Mean	Per cent P_2O_5 Up	Per cent P_2O_5 Down	Per cent P_2O_5 Mean	Ratio (Mean)	Per cent Di-salt from Ratio
0	7.69	7.62	7.66	16.28	16.28	16.28	0.470	96
10	9.89	9.85	9.87	20.70	20.61	20.66	0.478	99
20	10.54	10.46	10.50	21.94	21.89	21.92	0.480	100
30	10.87	10.89	10.88	23.00	23.00	23.00	0.473	97
40	11.45	11.46	11.46	24.47	24.55	24.51	0.467	95
50	12.06	12.20	12.13	25.41	25.34	25.38	0.478	99
60	12.58	12.55	12.57	26.80	26.90	26.85	0.468	95
70	13.07	13.22	13.15	27.58	28.01	27.80	0.473	97

Due to the decomposition which has taken place in some of the samples, there is sometimes a little doubt as to just how the percentage solubility should be calculated. In Table III is shown in Column 1 the solubility as calculated by dividing the mean ammonia percentage by 25.78, the theoretical percentage of ammonia in diammonium phosphate. Column 2 contains the solubility calculated in a similar manner from the P_2O_5 content of the solution, and Column 3 is the mean of Columns 1 and 2. The values of Column 3 are plotted in the accompanying graph (Fig. 3).

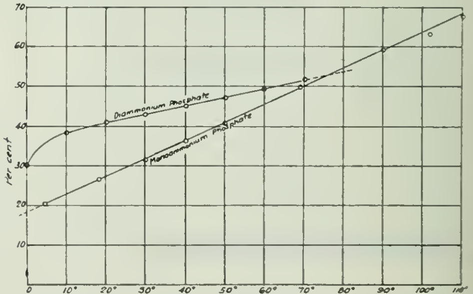

FIG. 3—THE SOLUBILITY OF MONO- AND DIAMMONIUM PHOSPHATES

As will be seen, the values between 10° and 70° C. lie in a straight line, and we derive therefrom the solubility formula:

Solubility Diammonium Phosphate (g. in 100 g. of the saturated solution between 10°–70° C.) = $36.5 + 0.213t$

The values of Column 4 are derived by calculation from this formula. Column 5 contains the values of Column 4, calculated as grams diammonium phosphate dissolved in 100 g. water.

Table III—Solubility of Diammonium Phosphate

	Grams Diammonium Phosphate				
	100 G. of Saturated Solution				100 G. Water
Temp. ° C.	(1)	(2)	(3)	(4)	(5)
0	29.7	30.3	30.0	..	...
10	38.3	38.4	38.4	38.6	62.8
20	40.7	40.8	40.8	40.8	69.0
30	42.2	42.8	42.5	42.9	75.2
40	44.4	45.6	45.0	45.0	81.8
50	47.0	47.2	47.1	47.2	89.2
60	48.8	49.9	49.4	49.3	97.3
70	51.0	51.8	51.4	51.4	106.0

SUMMARY

Solubility determinations made on the two commercially important phosphates of ammonia permit the derivation of the following solubility equations, representing the grams of the salt dissolved in 100 g. of the saturated solution between the temperature limits given:

Solubility Monoammonium Phosphate $^{5^\circ\text{ C.}}_{90^\circ\text{ C.}} = 18.0 + 0.455t.$

Solubility Diammonium Phosphate $^{10^\circ\text{ C.}}_{70^\circ\text{ C.}} = 36.5 + 0.213t.$

PEARL BARLEY: ITS MANUFACTURE AND COMPOSITION

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Received November 8, 1919

The barley crop of the United States approximates 200,000,000 bu. yearly, most of it being grown in North Dakota, California, Minnesota, South Dakota, Wisconsin, Kansas, and Iowa. The average annual yield per acre is about 25 bu. Heretofore fully one-third of the crop, or somewhat over 60,000,000 bu., has gone into malt for brewing and distilling, and a large amount is still malted for utilization in the manufacture of malt extract. About one-half of the crop is used directly as feed for animals, and from 2 to 3 per cent, or approximately 4,000,000 or 5,000,000 bu., is kept by the farmers for seed. This leaves a relatively small proportion of the entire crop (normally about 3,000,000 bu.) to go directly into human food as barley flour or pot and pearl barley. Except during the war, when a large portion of the crop was milled into a flour which was mixed with wheat flour and used for baking, barley has for the most part been consumed by man in the form of pearl or pot barley. In this form it has, of course, been used for many decades in Europe, particularly in Scotland where pot barley has met with special favor. About a score of manufacturers in this country are now engaged in making pearl barley, the total output of which before the war was 500,000 100-lb. sacks. The present paper contains the results of a study of the method of manufacture of pearl barley and of the chemical composition of the various products of the pearling operations carried out by the Plant Chemical Laboratory.

PEARL AND POT BARLEY

According to McGill,[1] the reduction in weight in producing pot barleys is 46 per cent. Such barley contains from 0.89 to 2.44 per cent of ash. The loss in making pearl barley is greater, as is evident from the fact that McGill finds that pearl barley contains from 0.58 to 1.27 per cent ash. Tibbles[1] states that Scotch barley is not decorticated as extensively as pearl barley. Church[2] states that from 100 lbs. of barley only 63 lbs. of pot barley, or about 32 lbs. of pearl barley, are obtained. Doubtless this pearl barley is the product resembling the fifth pearl barley of commerce. Gill[3] states that when the integuments of the barley are removed and the product rounded and polished the result is pearl barley.

Sometimes in the process of manufacturing pearl barley, sulfur dioxide is used to whiten the final product, and talc or similar substances are added to brighten and give it a "pearl-like" appearance. The amount of insoluble ash in normal pearl barley, which has not been subjected to the treatment with talc or other mineral substances, is less than 0.10 per cent. According to Liverage and Hawley[4] any sample of pearl barley containing a greater quantity of insoluble ash should be regarded as adulterated with mineral facing. Pluecker and Flebbs[5] have shown that the use of sulfur or talc is not for the purpose of preventing the growth of microörganisms, as has been claimed by some manufacturers, but is simply a commercial practice.

MANUFACTURE

The various steps to which barley is subjected in the pearling process are indicated in Fig. 1. The barley as first received is passed into storage bins from which it travels to automatic scales. The weighed grain is sent to the separator where it is partially cleaned by screens. From the separator it goes to the reel, which cleans it more thoroughly. The cleaning is completed by sieves and aspirators, after which the barley is ready for the pearling process. The grain

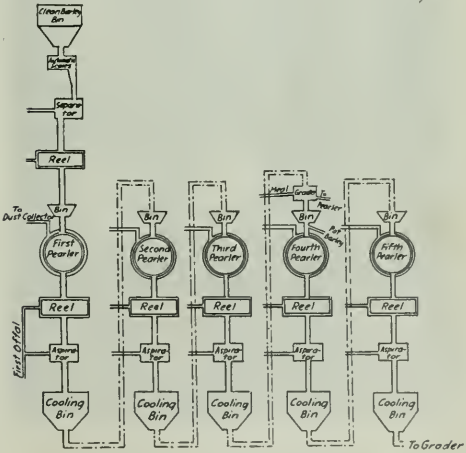

Fig. 1—Diagram Showing Barley Pearling Process

is carried from the cleaning devices, which differ in various mills, to the small bin over the first pearler.

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[1] Lab. Inland Rev. Dept., Ottawa, Canada, *Bulletin* **329**.

[1] "Foods, Their Origin and Manufacture," p. 471.

[2] "Food," p. 74.

[3] "Bread Maker," p. 75.

[4] *J. Soc. Chem. Ind.*, **34** (1915), 203.

[5] *Z. Nahr. Genussm.*, **28** (1914), 28.

The pearling machine used in the preparation of pearl barley generally consists of a large, vertical, cylindrical abrasive stone surrounded by a metal sieve, and resembles an ordinary grindstone in shape and position. The whole is enclosed in a dustproof metal jacket. The stone, usually of corundum, carborundum, or emery, may be as much as 4 ft. in diameter, and is made to revolve from 300 to 400 times per minute. The sieve surrounding this stone revolves about one-tenth as fast in the opposite direction. The barley, introduced automatically from a small bin or hopper, is subjected to a scouring action between the stone and the sieve. This abrasion continues for about 2 min., and the finer dust particles produced are removed from the enclosing jacket by means of dust collectors. The partly pearled barley and offal are then ejected, and a new charge of clean barley introduced. The entire process is automatic and practically continuous.

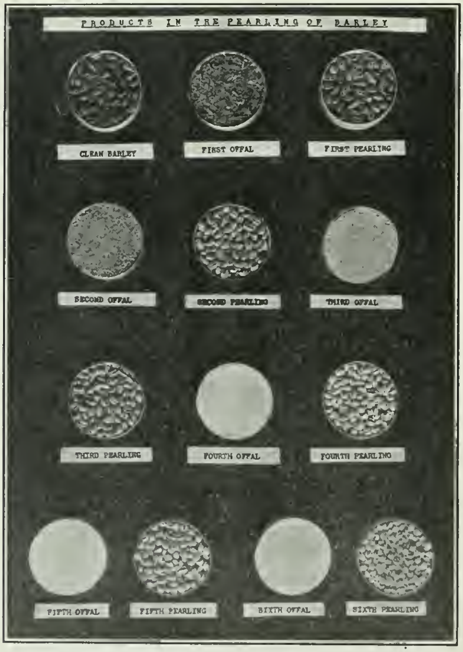

FIG 2

From the first pearler the mixture of offal and barley is sent to a reel which removes the offal or husk. From the reel the barley enters an aspirator where the remaining fine particles are removed. After cooling, the barley is ready for the second pearling.

The second operation, which is identical in process with the first, removes the next remaining layer of the grain, and the product thus obtained is likewise sent to a reel for the separation of the offal and the dust particles. The pearling is generally repeated from 4 to 6 times in order to remove by attrition all the outer coats of the barley grain.

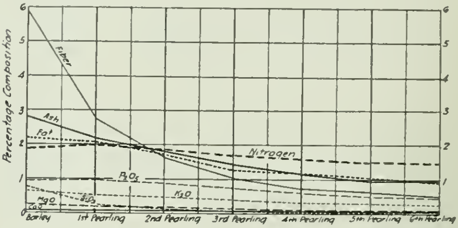

FIG. 3—COMPOSITION OF PEARLED BARLEY

After passing through the third process the partly pearled barley is often sent to a grader where it is assorted (Fig. 1). The large kernels are subjected to further attrition, thus producing a pearl barley of special type, the grain of which is rather large and well rounded. The smaller broken particles are collected and ordinarily used for feed. If the pearling process is stopped at the stage where only the outer cuticle is removed a "pot" barley (French, *Orge Mondé*) results. This is sometimes called Scotch barley, and is also known by various trade names. When the attrition is carried on still further a smaller type of pearl barley, which is generally separated into grades according to size, is produced. The different pot and pearl barleys and offal are shown in Fig. 2.

EXPERIMENTAL WORK

SAMPLES—Two sets of samples were obtained from a large cereal factory, one in 1916 and the other in 1917. In each case samples of the original barley, as well as of the products resulting from each pearling process, were collected. That is, the samples represent the original barley, the pearled or partly pearled barley, and the offal from each of the 6 pearling operations.

METHODS OF ANALYSIS—After grinding the samples so that they would pass through at least a 1-mm. sieve, they were analyzed for moisture, ash, protein, fat, and

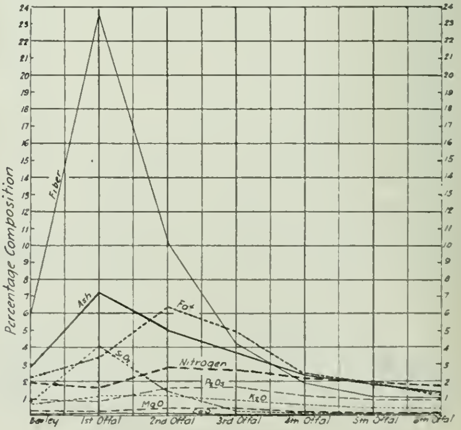

FIG. 4—COMPOSITION OF OFFAL

fiber, according to the methods of the Association of Official Agricultural Chemists. The constituents of the ash were determined as follows: P_2O_5 and K_2O according to the official methods of the Association of Official Agricultural Chemists; the silica also by the official method, except that it was not separated from carbon and sand, the amounts of which were so small as to be negligible. The calcium and magnesium were determined according to the McCrudden method,[1] with slight change in that it was not found necessary to boil the calcium solution during any part of the determination.

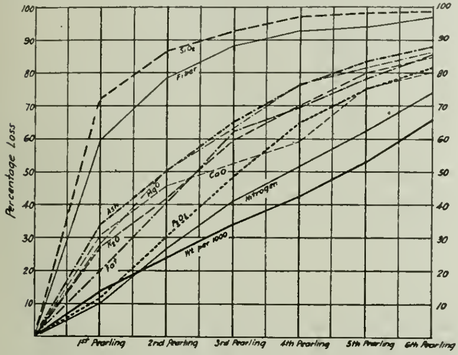

FIG. 5—PERCENTAGE LOSS OF CONSTITUENTS DURING PEARLING PROCESS

TABLE I—PERCENTAGE COMPOSITION ON DRY BASIS OF PEARL BARLEY AND OFFAL (5 Operations)

			Constituents								
Description	P. C. No.	Wt. per 1000 Kernels G.	Ash	Protein (N × 6.25)	Fat	Fiber	P_2O_5	K_2O	CaO	MgO	SiO_2
Original barley	18408	28.32	2.81	12.06	2.22	5.89	0.962	0.654	0.074	0.265	0.785
1st offal	18410		7.25	10.37	3.45	23.50	0.842	1.170	0.117	0.284	4.080
1st pearling	18411	24.37	2.15	12.56	2.07	2.76	0.984	0.553	0.059	0.221	0.257
2nd offal	18413		5.05	18.00	6.43	10.17	1.632	1.180	0.119	0 438	1.470
2nd pearling	18414	21.44	1.80	11.69	1.73	1.67	0.881	0.501	0.052	0.173	0.138
3rd offal	18416		3.73	17.12	4.98	4.28	1.691	0.977	0.092	0.448	0.259
3rd pearling	18417	18 72	1.44	10.75	1.26	1.04	0.744	0.400	0.053	0.146	0.069
4th offal	18419		2.42	13.81	2.43	1.93	1.180	0.609	0.070	0.282	0.210
4th pearling	18420	16.18	1.15	10.13	1.16	0.75	0.606	0.340	0.052	0.108	0.038
5th offal	18422		1.86	12.31	1.90	1.15	0.923	0.496	0.063	0.186	0.098
5th pearling	18421	13.20	0.96	9.69	1.02	0.65	0.506	0.276	0.039	0.102	0.029

RESULTS OF ANALYSIS—As has been stated already, from 4 to 6 pearling operations are necessary to secure a well-rounded, white, pearl barley. Tables I and II (P. C. 18408 and 18422) show the results of the analysis of pearl barley and the products of pearling obtained through 5 operations. Tables III and IV (P. C. 17575 and 17585) give similar results on products obtained from 6 pearling operations. These results are also graphically represented by the curves shown in Figs. 3, 4, and 5.

TABLE II—LOSSES DUE TO PEARLING (5 Operations)

Calculated from Weights Taken at the Mill[1]

			Constituents (Per cent)								
Description	P. C. No.	Wt. per 1000 Kernels G.	Ash	Protein	Fat	Fiber	P_2O_5	K_2O	CaO	MgO	SiO_2
1st pearling	18411	11.5	30.0	8.0	17.6	58.6	9.4	25.2	29.7	26.0	71.1
2nd pearling	18414	22.1	49.2	25.0	39.7	77.9	28.7	40.4	45.8	49.0	86.3
3rd pearling	18417	30.9	63.6	38.5	60.1	87.8	46.4	57.6	50.0	61.9	93.9
4th pearling	18420	38.1	74.5	48.3	67.8	92.1	60.9	67.9	56.7	78.5	97.0
5th pearling	18421	48.1	81.7	58.7	76.1	94.3	72.6	78.1	73.0	80.0	98.3
Calculated from Weight per 1000 Kernels											
1st pearling	...	13.7	34.1	10.3	19.8	59.8	12.0	27.2	31.1	28.3	71.8
2nd pearling	...	24.3	50.6	26.8	40.9	78.6	30.7	42.0	45.0	50.5	86.7
3rd pearling	...	34.2	65.3	41.2	62.4	88.3	48.7	59.5	52.7	63.4	92.8
4th pearling	...	42.8	76.4	51.9	70.0	92.7	64.9	70.2	59.4	76.6	97.2
5th pearling	...	53.0	83.5	62.7	78.2	94.8	75.3	80.2	75.7	81.9	98.2

[1] A complete charge from one of the pearling machines, consisting of from 50 to 100 lbs. of mixed barley and offal, was secured from each pearling operation. The pearl barley was separated from the offal, and the percentage loss calculated.

TABLE III—PERCENTAGE COMPOSITION ON DRY BASIS OF PEARL BARLEY AND OFFAL (6 Operations)

			CONSTITUENTS						
DESCRIPTION	P. C. No.	Wt per 1000 Kernels. G.	Ash	Protein (N × 6.25)	Fat	Fiber	P_2O_5	K_2O	CaO
Original barley..	17575	42.50	2.82	13.19	2.09	5.08	1.02	0.66	0.062
1st offal........	17577		6.89	10.56	2.77	23.74	0.97	1.12	0.095
1st pearling.....	17576	39.66	2.17	12.94	2.02	2.36	1.07	0.59	0.048
2nd offal.......	17579		5.13	19.56	6.48	9.25	1.92	1.15	0.097
2nd pearling....	17578	34.10	1.80	12.56	1.47	1.37	0.94	0.50	0.043
3rd offal........	17581		3.93	16.38	4.92	4.81	1.81	1.03	0.076
3rd pearling....	17580	30.40	1.45	10.25	1.19	0.91	0.81	0.41	0.035
4th offal........	17583		2.68	14.38	2.58	2.06	1.37	0.70	0.052
4th pearling....	17582	24.52	1.20	10.50	0.91	0.73	0.68	0.34	0.033
5th offal........	17585		2.13	13.45	2.04	1.35	1.14	0.58	0.047
5th pearling....	17584	20.13	1.06	10.37	0.94	0.58	0.62	0.32	0.030
6th offal.......	17585-*y*		1.67	12.50	1.67	1.22	1.00	0.47	0.038
6th pearling....	17585-*x*	14.25	0.98	9.44	0.89	0.44	0.56	0.30	0.035

TABLE IV—LOSSES DUE TO PEARLING (6 Operations)

Calculated from Weight per 1000 Kernels

		Constituents (Per cent)						
DESCRIPTION	Wt. per 1000 Kernels G.	Ash	Protein (N × 6.25)	Fat	Fiber	P_2O_5	K_2O	CaO
1st pearling.......	6.7	28.0	8.5	9.6	56.7	2.2	17.0	24.2
2nd pearling.......	19.8	48.9	23.7	43.5	78.4	26.2	39.8	45.1
3rd pearling.......	28.4	63.1	44.6	59.3	87.2	43.4	55.3	58.0
4th pearling.......	42.3	75.5	54.1	74.9	91.7	61.7	70.3	69.3
5th pearling.......	52.7	82.2	62.7	78.7	94.6	71.4	77.2	77.4
6th pearling.......	66.5	88.4	74.4	85.7	97.1	81.8	85.1	80.6

DISCUSSION OF RESULTS—From the chemical and physical study of the products of pearling, it is obvious that the offal resulting from the first pearling process (P. C. 18410 and 17577) is composed almost entirely of the hulls of the barley (Fig. 2). This offal has relatively little food value for man, both because of its extremely high content of fibrous material and of silica (23.6 per cent on an average for fiber and 4.1 per cent for the silica), and because of its physical characteristics. There is no doubt, however, but that there is some value as animal feed in the offal, even from the first pearling, because it contains an average of approximately 10.50 per cent of protein (N × 6.25) and an average of 3.11 per cent fat. The offal from the second-pearling (P. C. 18413 and 17579) contains over 18.75 per cent protein, 6.45 per cent fat, 9.70 per cent of fiber, and less than 1.5 per cent

TABLE V—PERCENTAGE OF MINERAL CONSTITUENTS IN ASH

		Constituents				
DESCRIPTION	Total Ash	P_2O_5	K_2O	CaO	MgO	SiO_2
Original barley......	2.82	36.2	23.4	2.2	...	...
	2.81	34.2	23.3	2.6	9.4	27.9
1st offal............	6.89	14.1	16.2	1.4	...	...
	7.25	11.6	16.1	1.6	3.9	56.3
1st pearling.........	2.17	49.3	27.2	2.2	...	...
	2.15	45.8	25.7	2.8	10.3	11.8
2nd offal...........	5.13	37.4	22.4	1.9	...	...
	5.05	32.3	23.4	2.3	8.7	29.1
2nd pearling........	1.80	52.2	27.8	2.4	...	...
	1.80	49.2	27.8	2.9	9.6	7.7
3rd offal............	3.93	46.1	26.2	1.9	...	...
	3.73	45.3	26.2	2.5	12.0	6.9
3rd pearling........	1.45	56.0	28.4	2.4	...	...
	1.44	51.6	27.7	3.7	10.1	4.8
4th offal............	2.68	51.1	26.1	1.9	...	...
	2.42	48.8	25.2	2.9	11.6	8.7
4th pearling........	1.20	56.6	28.3	2.7	...	...
	1.15	53.6	29.6	4.6	9.4	3.4
5th offal............	2.13	53.5	27.2	2.2	...	...
	1.86	49.6	26.7	3.3	10.0	5.2
5th pearling........	1.06	58.5	30.2	2.8	...	...
	0.96	52.7	28.7	4.0	10.6	3.0
6th offal............	1.67	59.9	28.1	2.3	...	...
	...	...	...	..	...	...
6th pearling........	0.98	57.1	30.6	3.6	...	...
	...	. .	...	..	...	..

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[1] *J. Biol. Chem.*, **7** (1909), 98; **10** (1911), 187.

SiO_2. The high content of P_2O_5 (over 32 per cent of the ash (Table V)), together with the high percentage of fat and protein, indicates that this offal is made up to a marked degree of the aleurone layer, or the so-called protein layer, a substance rich in protein, fat, and mineral ingredients. The second offal contains less than half as much fiber and about one-third as much SiO_2 as does the first offal. In addition, it contains twice as much fat and almost twice as much protein. A significant fact is the difference in ash constituents. The second-pearling offal contains less ash than does the first offal, but at the same time it contains twice as much P_2O_5, besides being much poorer in silica. All this shows that while at least two processes of pearling are essential for the production of an edible product, even this second pearling operation removes an appreciable amount of food constituents.

The third offal is also rich in protein, fat, ash, and P_2O_5, as well as in fiber. That this fiber is composed chiefly of the bran coating, however, and not of the hulls may be assumed from the relatively low silica content, and from the high P_2O_5 content of the ash of this product.

The edible product obtained from the third pearling operation, or the pot barley, is almost entirely free from the aleurone layer, as is evident from the low percentage of fat, fiber, and ash (Nos. 18417 and 17580 in Tables I and III). The fourth and fifth pot barleys are not only whiter, but are practically free from all bran material. They are still poorer in fat, fiber, and minerals than the pot barley from the third operation. The fifth pearl barley contains about one per cent each of ash and fat, and 0.6 per cent fiber. The ash contains a very high amount of P_2O_5 and a very low amount of SiO_2. The fourth offal contains about 2.5 per cent each of ash and fat, about 2.35 per cent nitrogen, and 2 per cent fiber, while the fifth offal still has about 2 per cent ash, nitrogen, and fat, and about 1.25 per cent fiber.

From Table V it is evident that the amount of SiO_2 in the ash in the first offal is over 56 per cent, and that it decreases rapidly, the offal after the second operation containing but a small amount of silica. The ash of the third offal is composed of only about 8 per cent SiO_2, while that of the fifth contains only 5 per cent. On the other hand, the percentage of P_2O_5 gradually increases from 11 per cent in the first offal to over 50 per cent in the fifth. The high P_2O_5 content and the low percentage of SiO_2 may well be considered a criterion of the quality of the product.

Tables I and III also show that the second-process pot barley (P. C. 18414 and 17578), which is practically free from hulls and constitutes the first product of the pearling process fit for human consumption, has, on the water-free basis, the following average percentage composition:

Ash	1.80
Nitrogen	1.94
Fat	1.60
Fiber	1.52
P_2O_5	0.91
K_2O	0.50
CaO	0.048
MgO	0.17
SiO_2	0.138

This is essentially the same as the composition of hull-less barley. With each process of pearling the percentage of nitrogen, fat, fiber, and the ash constituents gradually decreases. The fifth-pearling barley contains in per cent approximately:

Ash	1.00
Nitrogen	1.60
Fat	1.00
Fiber	0.60
P_2O_5	0.56
K_2O	0.30
CaO	0.035
MgO	0.10
SiO_2	0.03

Table VI shows how regularly the weights of the barley and of the food constituents are distributed as the result of the successive operations in the making of pearl barley.

TABLE VI—APPROXIMATE LOSSES DUE TO THE VARIOUS PEARLING OPERATIONS

	PEARLING						Difference between 2nd and 6th Pearlings
PER CENT LOSS IN	1st	2nd	3rd	4th	5th	6th	
Weight per 1000 kernels	10	22	31	42	53	66	44
Mineral ingredients	31	50	64	76	83	88	38
Nitrogen	9	25	43	53	62	74	49
Fat	15	41	60	72	78	85	44
Fiber	57	78	88	91	94	97	19
P_2O_5	7	28	45	62	73	83	55
K_2O	22	40	57	70	78	85	45
CaO	27	45	55	64	76	80	35
MgO	28	50	63	76	82	..	32
SiO_2	72	86	93	97	98	..	12

Assuming that 5,000,000 bu. of barley are now being yearly converted into pearl barley, the figures given in Table VII represent the weight of barley material and of the food constituents removed as the results of the two essential pearling operations and of the four subsequent processes. These figures mean that if all these 5,000,000 bu. of barley were passed through the 6 operations of the pearl barley process, as against the 2 operations necessary to make pot barley, 52,000 tons of barley material, containing over 6,700 tons of protein, over 1,000 tons of fat, and 1,100 tons of mineral ingredients, would be removed.

TABLE VII—APPROXIMATE AMOUNT OF BARLEY AND OF BARLEY CONSTITUENTS REMOVED BY PEARLING (IN TONS)

	Weight in Original Barley	Weight in Pearlings						Diff. in Weight between 2nd and 6th Pearlings
LOSS IN		1st	2nd	3rd	4th	5th	6th	
Weight	120,000	12,000	26,400	37,200	50,400	63,600	79,200	52,800
Mineral ingredients	3,000	930	1,500	1,920	2,280	2,490	2,640	1,140
Protein	13,650	1,229	3,412	5,896	7,234	8,463	10,159	6,747
Fat	2,330	350	955	1,374	1,677	1,817	1,979	1,025
Fiber	5,920	3,374	4,620	5,215	5,385	5,563	5,740	1,124
P_2O_5	1,068	75	299	481	662	780	886	587
K_2O	702	154	281	400	491	547	597	316
CaO	74	20	33	41	47	56	59	26
MgO	288	80	144	181	220	236	...	92
SiO_2	847	593	707	765	798	806	...	100

The figures in Table V show, moreover, that the first 2 pearlings are sufficient to remove practically all of the hull- and silica-containing portions of the barley, or the portions of the barley which are recognized as being unfit for human food. This is evident from the fact that 78 per cent of the fiber and over 85 per cent of the silica are removed in the course of these first 2 pearling operations. It is interesting to observe that the offal from the sixth pearling has essentially the same composition as the pot barley resulting from the second pearling process (Table III, P. C. Nos. 17585-y and 17578). This indicates that the offal from the sixth pearling might properly be used as a barley flour.

SUMMARY

Pot barley results from the gradual elimination of the outer layers of the barley (chiefly the husk and bran) which is accomplished in from 2 to 3 pearlings. From 5 to 6 pearling operations, in which a certain amount of endosperm, in addition to the husk and bran, is eliminated, are necessary to make pearl barley a white pearl-like product. Chemical analyses of all the products obtained in the manufacture show that the first two operations of pearling, resulting in pot barley, consist in the removal of most of the husk which carries with it three-fourths of the fiber and seven-eighths of the silica. These two operations, considered essential in order to remove the portions which cannot be used as a food, cause a loss of 22 per cent of the barley material, 25 per cent of the protein, 41 per cent of the fat, and 50 per cent of the mineral constituents. In continuing the operations to produce pearl barley the following constituents of the grain are removed: 65 per cent of the barley material; 74 per cent of the protein; from 80 to 85 per cent of the fat, P_2O_5, K_2O, CaO, and MgO; and from 97 to 98 per cent of the fiber and SiO_2. Assuming that 5,000,000 bu. of barley are being pearled yearly, 52,000 tons of barley material, consisting of over 1,000 tons each of fat and mineral ingredients and 6,700 tons of protein, are removed.

EFFECT OF VARYING THE AMOUNT OF INOCULUM AND CONCENTRATION ON THE DETERIORATION OF SUGAR BY MOLDS[1]

By Nicholas Kopeloff

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In a previous paper[2] it was shown that a decrease in concentration of films of known concentration in laboratory-made sugars was responsible for an increase in deterioration when heavily inoculated with mold spores. The industrial application of this conclusion is determined by two important variable factors, namely, the concentration of the films surrounding the sugar crystals, and the degree of infection. Therefore, a further investigation of the influence of these factors was considered necessary.

The method of procedure was identical with that outlined in the previous article, except that the incubation period was 5.5 mo. instead of one month. A series of sugars with films of known composition was made in the laboratory by coating large crystals of sterilized sugar with sterilized blackstrap molasses and 60° Brix sugar sirup in definite proportions and purging in the centrifugal, a method previously employed with success. Blackstrap molasses, $^6/_6$ blackstrap + $^1/_6$ sirup, $^4/_6$ blackstrap + $^2/_6$ sirup, and $^3/_6$ blackstrap + $^3/_6$ sirup when arranged in order of increasing moisture ratio are designated as Concentrations A, B, C, and D, respectively. These sugars were inoculated with *Aspergillus niger*, *Aspergillus* Sydowi Bainier and *Penicillium expansum*, at the rate of 100, 1000, and 10,000 spores per gram. At the end of 5.5 mos. incubation at room temperature the contents of each flask were analyzed for sucrose by direct polarization and modified Clerget, and for reducing sugars and moisture. It has already been shown[1] that the most satisfactory criterion of deterioration of sugar is the gain in per cent of reducing sugars. In order to summarize the results as briefly as possible, there is given in Table I the increase over check of the averages of closely agreeing triplicate determinations of reducing sugars. The abbreviation M. R. stands for moisture ratio, which value is derived as follows: M. R. = $\frac{\text{Moisture}}{100 - \text{Polarization}}$; *Asp. n.* is the abbreviation for *Aspergillus niger*, while *Asp.* S. B. and *Pen.* represent *Aspergillus* Sydowi Bainier, and *Penicillium expansum*.

TABLE I—SUMMARY SHOWING THE INFLUENCE OF AMOUNT OF MOLD INOCULUM ON THE DETERIORATION OF SUGARS WITH FILMS OF KNOWN CONCENTRATION. INCREASE IN PER CENT REDUCING SUGARS OVER CHECK

	CONCENTRATION											
	A M. R. = 0.14			B M. R. = 0.16			C M. R. = 0.18			D M. R. = 0.24		
No. Spores per Gram	*Asp. n.*	*Asp.* S. B.	*Pen*	*Asp. n.*	*Asp.* S. B.	*Pen.*	*Asp. n.*	*Asp.* S. B.	*Pen.*	*Asp. n.*	*Asp.* S. B.	*Pen.*
100	..	..	..	..	0.09	0.01	..	0.09	0.07	..	0.10	0.10
1000	..	0.02	0.02	..	0.05	0.04	0.12	0.22	0.17	0.04	0.18	0.18
10,000	0.04	0.21	0.11	0.03	0.12	0.11	0.27	0.31	0.28	0.12	0.27	0.28

It will be seen from this table that in every instance but one an increase in the number of spores per gram caused an increase in per cent of reducing sugars over check. This held true not only at every concentration employed, varying in moisture ratio from 0.14 to 0.24, but likewise for every organism used at any single concentration. This fact is very significant and indicates conclusively that an increase in degree of inoculation of mold spores at any definite concentration is responsible for an increase in deterioration of sugar. This corroborates our previous work where solutions varying from 10 to 70 per cent were employed,[2] as well as the results obtained in the experiment just concluded,[3] where an inoculation of 100,000 spores per gram at each of the above-mentioned concentrations was employed. A closer scrutiny of the results presented in Table I reveals the fact that the increase over check of reducing sugars with an inoculation of 100 spores per gram is insignificant at practically all concentrations. The same is true of an inoculation of 1000 spores in the two higher concentrations, namely, A and B. This is of practical importance in defining the limits at which deterioration occurs, since in plantation granulated sugars the moisture ratio may be said ordinarily to be below 0.18. It is generally considered that good Cuban raw sugar likewise should have its moisture ratio below 0.25 to 0.33. Thus, it might be inferred from the foregoing data that where the moisture ratio is below 0.18, mold infection of less than about 5,000 spores per gram would cause slight, if any, deterioration. As a rule we have rarely found sugars which had more than 250 mold spores per gram, although no quantitative survey has been carried out as exhaustively as might have been desirable.

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[1] Read before the Louisiana Section of the American Chemical Society, November 21, 1919.

[2] THIS JOURNAL, **12** (1920), 256.

[1] *Louisiana Bulletin* **166**.

[2] *J. Agr. Res.*, **18** (1920), 537.

[3] THIS JOURNAL, *Loc. cit.*

When the two lower concentrations C and D are considered, we find that there is evidence of deteriorative activity with 100 spores per gram, while with more than 1000 spores the deterioration is quite appreciable. It would appear, therefore, that for safety (from the standpoint of mold infection) a sugar having a moisture ratio of 0.17 to 0.18 would have to contain less than 100 mold spores per gram. On the other hand, a mold infection of more than 10,000 spores per gram will cause a deterioration in sugars with moisture ratios varying from 0.14 to 0.24. It may be noted in this connection that in the previous investigation an inoculation of 100,000 spores per gram was responsible in one month for a deterioration in sugars with moisture ratios varying from 0.08 to 0.20.

An interesting fact which corroborates all our previous work with sugars, as well as solutions, is that at any definite concentration and with an equal number of spores per gram *Aspergillus* Sydowi Bainier is more effective than *Penicillium expansum*, which in turn is more effective than *Aspergillus niger* in deteriorative activity.

TABLE II—SUMMARY SHOWING THE INFLUENCE OF CONCENTRATION OF FILM ON DETERIORATION OF SUGARS BY MOLDS

		—Per cent Gain in Reducing Sugars over Check—								
		100 Spores per G.			1000 Spores per G.			10,000 Spores per G.		
Concentration	Moisture Ratio	*Asp. n.*	*Asp.* S. B.	*Pen.*	*Asp. n.*	*Asp.* S. B.	*Pen.*	*Asp. n.*	*Asp.* S. B.	*Pen.*
A	0.14	..	..	..	..	0.02	0.02	0.04	0.21	0.11
B	0.16	..	0.09	0.01	..	0.05	0.04	0.03	0.12	0.11
C	0.18	..	0.09	0.07	0.12	0.22	0.17	0.27	0.31	0.28
D	0.24	..	0.10	0.10	0.04	0.18	0.18	0.12	0.27	0.28

In Table II is presented a summary of results so arranged as to show the influence of concentration of film on the deterioration of sugars by molds. It must be stated at the outset, however, that where the increasing increments of moisture are so slight as in the present instance, and especially when dealing with the activity of microörganisms over such a long incubation period, it is hardly to be expected that the differences will be very sharply defined. However, it will be observed that as a rule an increase in moisture ratio (which actually signifies a decrease in concentration) is responsible for an increase in deterioration with any single inoculation. It is not necessary to repeat here what was stated in the discussion of Table I concerning the limiting effects of concentration with any definite inoculum. Suffice it to say that this work fits in very closely with our preceding investigations and proves quite conclusively that with a high mold infection, deterioration takes place in sugars with moisture ratios below 0.14, or, according to the previous experiment, at 0.08. This substantiates the claim previously made that "the factor of safety for sugars well infected with fungi would appear to be lower than is generally supposed," and defines more clearly what such limits must be. In other words, knowing the number of molds present in any sugar, it may be predicted (from the standpoint of mold infection alone) what deterioration may be expected in a storage period of about 5 mo. with a sugar of known moisture ratio. It is to be assumed that at the present time sugars are not stored for such a long period of time, but the differences obtained upon a long incubation period are not so much greater as to invalidate the above generalizations, as will be seen from Table III, which gives a comparison in the reducing sugar content of inoculated sugars with films of Concentration D (moisture ratio = 0.24) after 1 and 5.5 mo., respectively. It will be readily seen that the differences in incubation as represented by the gain in per cent of reducing sugars are indeed slight when compared with the initial gain over check in one month.

TABLE III—COMPARISON IN CONTENT OF REDUCING SUGARS OF INOCULATED SUGARS (WITH FILMS OF CONCENTRATION D) AFTER 1 AND 5.5 MOS. INCUBATION, RESPECTIVELY

Incubation	Check	*Asp. n.*	Gain over Check	*Asp.* S. B.	Gain over Check	*Pen.*	Gain over Check
After 1 mo.	0.23	0.44	0.21	1.10	0.87	0.77	0.54
After 5.5 mo.	0.23	0.53	0.30	1.46	1.23	0.87	0.64
Gain in reducing sugars, per cent	0.00	0.09	..	0.36	..	0.10	..

Next to the elimination of deterioration, the most important commercial consideration is prediction of the keeping quality of a sugar. Table IV is a tentative plan based on the results obtained in all our investigations which will give some conception of the deterioration to be expected from a definite number of molds in sugars of known moisture ratio. It must be clearly understood that this plan is advanced with considerable diffidence, and that its value rests on further verification. Furthermore, it is of importance to note that in the above table mold infection only has been considered. We have data which are concerned with deterioration due to bacterial infection and unquestionably the bacterial flora would seriously influence the deterioration of sugars as shown in the important researches of previous investigators. However, since individual molds, such as *Aspergillus* Sydowi Bainier, *Penicillium expansum*, and *Aspergillus niger*, are vastly more efficient in their deteriorative activity than any bacteria that have come to our attention, and since the first-named mold is to be found in practically all sugars, it may be that the above table will prove of some value to those who are ready to take cognizance of the molds which are undoubtedly causing large economic losses in the sugar industry. In Table IV it will be seen that the facts previously discussed have been so arranged that one may tell at a glance what deterioration, if any, might be expected. It was not deemed necessary to carry out the work in moisture ratios beyond 0.24, because it is generally conceded that sugars having a moisture ratio above 0.30 are

TABLE IV—DETERIORATION TO BE EXPECTED FROM A DEFINITE NUMBER OF MOLDS IN SUGARS OF KNOWN MOISTURE RATIO

$$\text{Moisture Ratio} = \frac{\text{Moisture}}{100 - \text{Polarization}}$$

No. of mold spores per g.	0.08	0.14	0.16	0.18	0.20	0.24	Over 0 24
0–100	—	—	±	+	+	+	+
100–1000	—	±	±	+	+	+	+
1000–10,000	±	+	+	+	+	+	+
10,000–100,000	+	+	+	+	+	+	+

+ Deterioration
— No deterioration
± Slight, if any deterioration

susceptible to deterioration. Browne,[1] Owen,[2] and others have advanced much valuable evidence on this point.

This paper may be said to round out one phase of the problem of sugar deterioration, namely, that concerned with the importance of mold infection, which we have carried through to completion, from a survey of mold species in sugar and their deteriorative activities in sugars and solutions to a study of the effect of varying the amount of inoculum and concentration on deterioration.

The writer wishes to thank Messrs. D. F. Stanfill, Jr., and R. S. Hays for their help with the chemical analyses and the Station staff for their assistance, and is indebted to Mr. W. L. Owen for his kindness in reading the manuscript.

SUMMARY

1—An increase in number of mold spores inoculated into sugars (with films of varying concentration) is responsible for an increase in deterioration.

2—A decrease in concentration of the films surrounding the sugar crystals is responsible for an increase in deterioration.

3—A table is presented showing the deterioration which may be expected from a definite number of molds in sugars of known moisture ratio.

4—At moisture ratios of less than 0.18 there is little, if any, deterioration with a mold infection of less than 5,000 spores per gram. More than this number of spores induces deterioration. At moisture ratios above 0.18, deterioration occurs with upwards of 100 spores per gram.

5—At any definite concentration and with an equal number of spores per gram *Aspergillus* Sydowi Bainier is more effective than *Penicillium expansum* or *Aspergillus niger* in its deteriorative activity.

ACIDITY AND ACIDIMETRY OF SOILS.[3] II—INVESTIGATION OF ACID SOILS BY MEANS OF THE HYDROGEN ELECTRODE

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Received October 14, 1919

INTRODUCTION

Although the literature upon the subject of soil acidity is voluminous, the use of the hydrogen electrode in soil investigations has been rather limited.

Gillespie[4] made use of the hydrogen electrode for determining the hydrogen ion concentration of a mixture of soil with pure water; but, for reasons which will develop in the investigations given herewith, the presence of a conducting medium was found to be desirable. Sharp and Hoagland[5] studied the hydrogen concentrations of suspensions of soils in pure water under various conditions, effects of natural salts and bases upon hydrogen ion concentrations of soil suspensions, and made titrations with various bases.

The purpose of the present investigation is to study: (1) the speed of reactions between neutral salt solutions and soils; (2) the speed of reactions in the presence of a base; (3) the change in hydrogen ion concentration with change of amount of base and with time, and the change in conductivity of soil solutions.

APPARATUS

Preliminary experiments were conducted with an apparatus similar to that described by Hildebrand,[1] and some experiments described elsewhere with soil solutions were carried out, but for use with solutions in contact with the soil it was found to be rather unsatisfactory. For all work reported, unless otherwise stated, a high-grade potentiometer (Leeds and Northrup, No. 28952) was used with a gas cell especially designed for the work.

GAS CELL—Preliminary experiments showed that for uniform results it was necessary to have a gas cell which could be agitated continuously, as apparently the agitation produced by the entering gas was not sufficient. After a number of trials the gas cell shown in Fig. 1 was designed for this work. It is cylindrical in shape, 3.3 cm. in diameter and 16 cm. in length, the ends being rounded off. At one end an opening is provided of a size to carry a No. 4 rubber stopper, through which pass the electrical connection *a* to the platinum plate *b* to serve as the hydrogen electrode, the tube *c* for the ingress of hydrogen gas, and tube *d* for the outlet. Tubes *c* and *d* have capillary tubes sealed into the ends to regulate the flow of hydrogen. To make connections with the calomel half cell a glass tube, *g*, is provided at the further end of the gas cell provided with a stopcock, *f*, and a constricted tip, *h*. This tube reaches to within a few mm. of the bottom of the gas cell and as it did not readily clog with soil was found to be very satisfactory. The gas cell was designed to be of 100 cc. capacity and to be filled half full of liquid, leaving room for 50 cc. of gas. The reason for this arrangement will develop later.

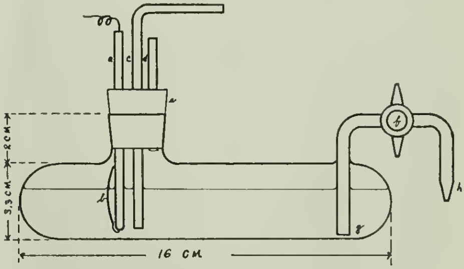

FIG. 1

The hydrogen electrode *b* is a rectangular piece of sheet platinum, 1.2 x 2.4 cm., with pieces of platinum wire welded to each end, and is similar to that used by

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[1] This Journal, **10** (1918), 178.

[2] *Louisiana Bulletin* **162**.

[3] This is a thesis submitted to the faculty of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Acknowledgment is made of many helpful suggestions and criticisms received from Prof. C. G. Hopkins and H. A. Noyes.

[4] *J. Wash. Acad. Sci.*, **6** (1916), 7.

[5] *J. Agr. Res.*, **7** (1916), 124.

[1] *J. Am. Chem. Soc.*, **35** (1913), 847.

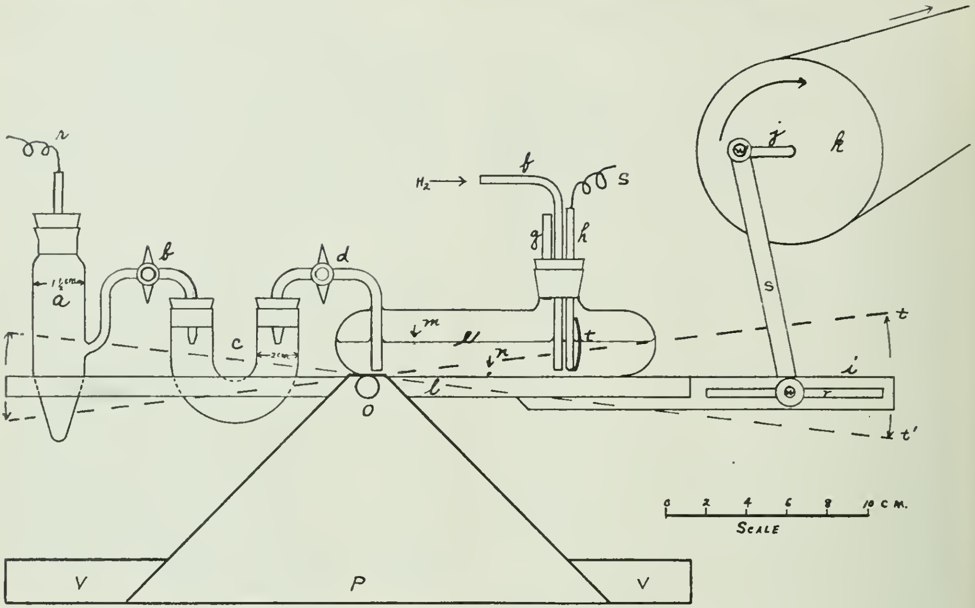

Fig 2.

Gillespie.[1] The wires were welded into the glass tube at each extremity as shown, making connections with the mercury in the tube and at the same time supporting the electrode rigidly.

Fig. 2 shows diagrammatically the method of agitating the cell and connections as measurements were being made. *a* is the calomel electrode provided with a stopcock, *b*, and *c* is a U-tube filled with normal potassium chloride, making connection with the hydrogen gas cell by the tube *d*. The apparatus was placed upon a tilting table hinged at the point *o* to the base *P*. The table is rocked by means of the adjustable arm *s* and crank *j* attached by suitable gears and pulleys to a constant source of power. In building up the shaking apparatus free use was made of the parts of one of the popular metal construction shapes to teach children to make their own toys.

It was found by experiment that by giving the table 72 complete oscillations per minute through a total angle of 6° to 7° the liquid in the gas cell was thoroughly agitated; that the rubber stopper was not wetted, but that the soil was kept thoroughly mixed with the solution while the coarser particles of sand in the soil would tend to collect in a nodal point *n* in the bottom of the cell near the center. At this speed the hydrogen bubbles rose to about the point *m* before they broke, causing the cell to be quickly freed of air. Except for very light peat soils there was no tendency for the soil to ascend into the tube *d*.

The arrangement of the different parts of the apparatus as used in making measurements is shown diagrammatically in Fig. 3. The apparatus is designed to carry two gas cells, marked E. M. F., so that duplicate measurements may be made without changing cells.

The use of the U-tube for making connections between the gas cells and calomel electrode was found to be a most satisfactory arrangement. The resistance of the chain is slightly increased, but diffusion is markedly reduced. During several weeks of continuous use, the calomel electrode changed less than 0.0005 volt. The gas cell is claimed to have the following advantages:

(1) large capacity, (2) absence of dead air space, (3) ease of cleaning, (4) all-glass contact with liquid, (5) freedom from clogging, (6) ease of manipulation, (7) adaptability to thorough agitation, (8) minimum possibility of diffusion.

CALOMEL ELECTRODE—Calomel was prepared by treating pure mercury with dilute nitric acid, precipitating with hydrochloric acid, washing twenty times with potassium chloride, and finally shaking with normal potassium chloride and pure mercury, as recommended by Ellis[1] for obtaining an electrode of constant potential. The electrodes were prepared with this gray mixture of mercury, calomel, and normal potassium chloride by first putting into the bottom of the carefully cleaned electrode cell a small amount of pure mercury to cover the platinum connection. No difficulty was experienced in getting electrodes to check within 0.0005 volt. The stopcock upon the tube leading from the calomel electrode was well greased and was opened only when readings were being taken. Connection was made to the U-tube *c* (Fig. 2) through a rubber stopper well driven home, making this side of the system practically gastight.

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[1] *Loc. cit.*

[1] *J. Am. Chem. Soc.*, **38** (1916), 737.

HYDROGEN ELECTRODE—The platinum electrode was prepared by plating as a cathode in a one per cent solution of platinum chloride, containing a small amount (about 0.05 per cent) of lead acetate to cause the platinum black to adhere. Attempts were made to use a solution of pure platinic chloride as recommended by Ellis, but this proved unsatisfactory as the platinum black invariably washed off within a few minutes after being placed in the cell.

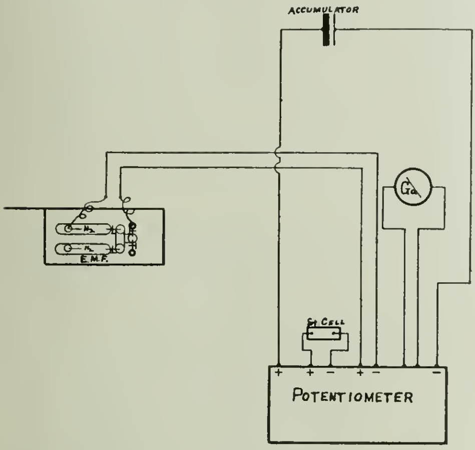

Fig. 3

In plating a platinum anode was used. The strength of the current was varied from time to time but no variation in the potentials of the electrode or in the time required to become saturated was noted from this cause. If the evolution of hydrogen was too lively some of the platinum black was loosened. The plating was continued from 1 to 2 hrs., or until a good heavy deposit of platinum black was formed. The electrodes were placed in distilled water and given a final wash just before using.

HYDROGEN GENERATOR—Hydrogen was prepared electrolytically as needed, using potassium hydroxide and nickel electrodes, as shown in Fig. 4. Two salt-mouth bottles, *G* and *G'*, were used. *E* and *E'* are the nickel electrodes, *M* and *M'* are glass partitions running almost to the bottom of the cells to reduce diffusion as much as possible. *P* and *P'* are safety valves made of test-tubes. The outlets *O* and *O'* were closed while hydrogen was being taken off. By using two cells in parallel and electrolyzing with a current of 10 amperes, about 150 cc. of hydrogen per minute were obtained. The usual general precautions were taken in washing and purifying the gas.

PROCEDURE

To fill the tube *g* of the gas cell (Fig. 1) the cell was partly filled with liquid, a stopper inserted in the opening *e*, and pressure exerted, so that, when the stopcock *f* was opened, the liquid would fill the tube *g* and flow out at *h*. Care was taken to thoroughly wet the stopcock *f* by loosening and turning. All measurements were made with this stopcock closed.

After the gas cell was filled with soil and solution and placed as shown in Fig. 2 the table was oscillated and hydrogen run in at *f* for 4 or 5 min.; the tube *g* was closed and rocking continued for 4 min.; hydrogen was again run in for 4 min. to drive out the last traces of air; *g* was again closed, the stopcock *b* opened, and readings were taken immediately.

The procedure varied somewhat with the number of readings to be taken, type of experiment, etc. If readings were to cover a period of half an hour or more, after the first large volume of hydrogen was run in, it was found advisable to allow a small amount to bubble through to overcome any diffusion which might take place through the rubber connections.

DESCRIPTION OF SOILS INVESTIGATED

Yellow-Gray Silt Loam, Sample No. 1—An acid subsoil collected from the southern part of the state of Illinois. This soil gave a lime requirement by the Hopkins method[1] of 4.2 tons and by the Veitch method[2] 5.6 tons calculated as calcium carbonate.[3] No carbonates were present as determined by the Marr[4] method.

Black Peaty Loam, Sample No. 1–281[5]—Collected by C. G. Hopkins near Bolton, N. C. Limestone requirement by the Hopkins method was 3.445 tons.

Black Clay Loam, Sample No. 1–284—Collected by C. G. Hopkins near Bolton and Byrdsville. Some leaf mold was present. Limestone requirement by the Hopkins method was 4.982 tons.

Peat, Sample No. 1–241—Labeled deep peat or muck, collected near Titusville, Florida, by C. G. Hopkins. Limestone required by the Hopkins method was 3.267 tons.

Black Muck, Sample No. 1–242—Collected from Wauchula, Florida, collected by C. G. Hopkins. Limestone requirement by the Hopkins method was 4.056 tons.

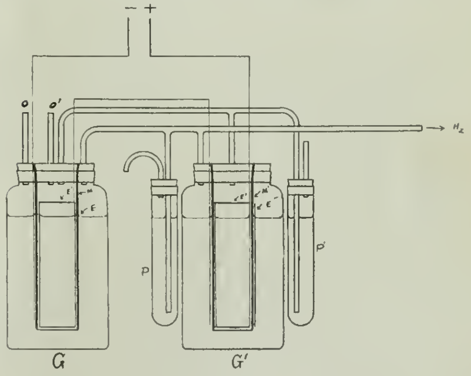

Fig. 4

Yellow Silt Clay, Sample No. 2660—Collected from Clay County, Illinois. A silty clay, stiff and plastic.

[1] U. S. Dept. of Agr., Bureau of Chem., *Bulletin* **107** Revised (1908), 20.

[2] *J. Am. Chem Soc.*, **24** (1902), 1120.

[3] All figures are based upon an acre of soil 6$^{2}/_{3}$ in. in depth, calculated to weigh 2,000,000 lbs., except peats which are calculated to weigh 1,000,000 lbs

[4] *J. Agr. Sci.*, [11], **3**, 155.

[5] Numbers refer to the University of Illinois Soil Survey Numbers.

Subsoil sample. Limestone required by the Hopkins method was 5.08 tons.

Gray Clayey Silt, Sample No. 2968—Collected from Jackson County, Illinois. A compact, impervious subsoil containing iron blotches and concretions. Limestone required by the Hopkins method was 7.92 tons.

Gray Plastic Clay, Sample No. 3957—Collected from Winebago County, Illinois. A subsoil sample containing clayey sand. Limestone required by the Hopkins method was 2.6 tons.

Yellow Plastic Clayey Silt, Sample No. 3556—Collected from Clay County, Illinois. A subsoil sample. Limestone required by the Hopkins method was 4.67 tons.

Yellow Silt Loam, Sample No. 4068—Collected from La Salle County, Illinois. This was subsurface sample having a lime requirement by the Hopkins method of 2.89 tons.

Brown Sandy Loam, Sample No. 6316—This was subsurface sample having a limestone requirement by the Hopkins method of 1.65 tons.

EXPERIMENTAL

EXPERIMENT I. SPEED OF REACTION BETWEEN AN ACID SOIL AND A NEUTRAL SALT—This experiment was planned to observe the speed of change in hydrogen ion concentration of a neutral salt solution when shaken together with an acid soil.

The gas cell was filled with 50 cc. of 0.5 *N* salt solution and after the potential had become constant, which was usually within 10 min., 5 g. of soil (2.5 g. in the case of peat soil) were quickly introduced and readings were taken at stated intervals.

TABLE I—SPEED OF REACTION BETWEEN ACID SOIL AND A NEUTRAL SALT SOLUTION

(Readings are given in volts. Temperature 25° C.)

	——Yellow-Gray Silt Loam——			Brown Sandy Loam	Yellow Plastic Clayey Silt	Peat
TIME MIN.	0.5 *N* KCl	1/4 Mol. $CaCl_2$	0.5 *N* $KC_2H_3O_2$	0.5 *N* KCl	0.5 *N* KCl	0.5 *N* KCl
0	0.6969	0.6823	0.7295	0.6966	0.6967	0.6967
5	0.4843	0.4947	0.6715	0.5658	0.4944	0.5706
10	0.4843	0.4950	0.6707	0.5660	0.4944	0.5691
15	0.4848	0.4950	0.6706	0.5660	0.4944	0.5687
20	0.4854	0.4950	....	....	0.4944	0.5687
25	0.4860	....	0.6693	....	0.4946	0.5688
30	0.4865	0.4950	....	0.5660	0.4946	0.5690
40	0.4871	....	0.6693	....	0.4950	0.5692
60	0.4878	0.4957	0.6693	0.5664	....	0.5696
90	0.4890	0.4963	....	....	....	....
120	....	....	....	0.5670	0.4969	....
180	0.4895	0.4972	0.6688	....	0.4984	....
240	....	....	....	....	0.5010	....
	0.4963[1]	....	....	0.5733[2]	0.5063[3]	....

[1] After 24 hrs. [2] After 48 hrs. [3] After 12 hrs.

Under the conditions of the experiment a voltage of 0.6967 represents a hydrogen ion concentration of 10^{-7} or true neutrality. Voltages less than this figure show a higher hydrogen ion concentration or a condition of acidity while figures above show a hydrogen ion concentration of less than 10^{-7} or an alkaline condition.

In Table I it will be noted that the lowest readings were obtained within 5 min. in all cases but two, the yellow-gray silt loam with potassium acetate, and peat with potassium chloride. The potassium acetate solution showed a marked alkalinity before the soil was added, therefore we should expect it to act more as a base. It will be discussed in connection with the next experiment. The peat did not wet readily which may account for its behavior. After the low readings were obtained there was a gradual increase in the voltages, corresponding to a decrease in the hydrogen ion concentration.

It is evident that the main reaction between the salt solution and the soil reaches an equilibrium very quickly. Secondary reactions are indicated by an increase in voltage after a lapse of time, except in the case where potassium acetate was used, where secondary reactions are not apparent to any great extent. Secondary reactions of greater or less magnitude should be expected when the hydrogen ion concentration rises appreciably above 10^{-7}. Reduction of nitrates[1] may be put forward as an explanation but this is immediately questioned since there is no evidence of the potassium acetate mixture showing a change toward alkalinity.

EXPERIMENT II. SPEED OF REACTION IN THE PRESENCE OF A BASE—This experiment was similar to Expt. I. 50 cc. of 0.5 *N* potassium chloride solution containing given quantities of calcium hydroxide, calculated as calcium carbonate, were used, as indicated in Table II. Five grams of soil were used except in the case of peat, when 2.5 g. were used.

TABLE II—SPEED OF REACTION BETWEEN SOIL AND SALT SOLUTION IN PRESENCE OF BASE

TIME MIN.	Brown Sandy Loam 2 T. $CaCO_3$	Yellow-Gray Silt Loam 4 T. $CaCO_3$	10 T. $CaCO_3$	Yellow Plastic Clayey Silt 5 T. $CaCO_3$	Peat 10 T. $CaCO_3$
0	0.9543	0.9715	0.9961	0.9803	0.9961
5	0.7783	0.7483	0.8505	0.6562	0.8345
10	0.7565	0.6923	0.8410	0.6302	0.7642
15	0.7440	0.6467	0.8363	0.6228	0.7370
20	0.7313	0.6161	0.8356	0.6199	0.7173
25	0.7269	0.6037	0.8337	0.6170	0.7053
30	0.7232	0.5978	0.8326	0.6148	0.6951
40	0.7165	0.5935	0.8298	0.6111	0.6809
60	0.7113	0.5897	0.8273	0.6072	0.6672
90	....	0.5855	0.8262	....	....
120	0.7066	....	....	0.5987	0.6499
180	....	0.5820	0.8206	0.5951	0.6432
	0.7022[1]	....	0.8186[2]	0.5933[3]	0.6394[3]

[1] After 48 hrs. [2] After 5 hrs. [3] After 4 hrs.

The change in the hydrogen ion concentration was very rapid at first, but continually rose as long as the experiments were conducted. The plotted curves are all similar in character and of the general type shown in Fig. 5, which is for the yellow-gray silt loam with four tons of lime.

Although equilibrium is not reached for a considerable period under the conditions of the experiment, the greater portion of the reaction takes place within a few minutes. After the neutral point is reached the hydrogen ion concentration continues to increase at the same relative rate without change. This phenomenon explains the condition noted by MacIntire[2] who distinguishes between immediate and continued lime requirement and Truog[3] who makes the division into active and latent soil acidity. Both investigators added an excess of lime to the soil while in certain of the above experiments the lime requirements were not satisfied. Apparently the reaction is in each case an equilibrium reaction. Such being the case, any division as indicated by them is an arbitrary one, and the results will not necessarily bear any relation to the total lime requirements.

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[1] An attempt was made to use potassium nitrate but it was noted that even in a neutral solution reduction of the nitrate to ammonia took place to an extent which could be noted with organic indicators.

[2] Tenn. Expt. Sta., *Bulletin* **107** (1914), 193.

[3] THIS JOURNAL, **8** (1916), 341.

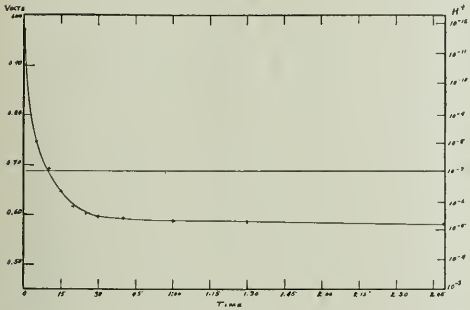

FIG. 5

It would seem from an inspection of the curve that the relation may be expressed empirically by the equation

$$\frac{dx}{dt} = K(A - x),$$

in which x is the hydrogen ion concentration with time t, A the total change in hydrogen ion concentration, and K a characteristic constant for the system under consideration. It would appear that the longer the interval chosen the more nearly would the results approach the maximum lime absorption, provided side reactions are not considered. It is quite probable that under field conditions the reactions will be far slower than the above experiment would indicate. The conditions in the field are often such that reactions cannot take place rapidly, while the converse is true in the laboratory. In this experiment a salt solution was used with calcium hydroxide, a condition, certainly, where reaction may take place with utmost speed.

This experiment would seem to throw some light upon the action of soil with potassium acetate in Expt. I. Potassium acetate is basic in character and even at the end of 180 hrs. the mixture with an acid soil contained only a slight excess of hydrogen ions.

EXPERIMENT III. STUDY OF CHANGE IN HYDROGEN ION CONCENTRATION OF NEUTRAL SALT SOLUTION CONTAINING VARYING AMOUNTS OF BASE—50 cc. of a 0.5 *N* neutral salt solution containing the desired amount of base were placed in the gas cell and readings were taken at the end of 20 min. The gas cell was rocked continuously as in the former experiments.

In the light of Expt. II, it can be readily understood that duplicates are somewhat difficult to obtain unless the manipulation is the same, and the time element eliminated. The speed of the reaction should depend somewhat upon the base used and the neutral salt with which it is combined. Considering these facts it is rather remarkable that the results obtained as shown in Table III should be of the same order. The experiments were all conducted upon yellow-gray silt loam.

TABLE III—STUDY OF CHANGE IN HYDROGEN ION CONCENTRATION OF A NEUTRAL SALT SOLUTION TO WHICH VARIOUS AMOUNTS OF BASE HAVE BEEN ADDED WHEN PLACED IN CONTACT WITH SOIL.

(Results given in volts. Soil is yellow-gray silt loam. 5 g were taken in each case)

Base Equivalent to T. $CaCO_3$	0.5 *N* KCl + $Ca(OH)_2$	0.5 *N* NaCl + $Ca(OH)_2$	0.5 *N* $CaCl_2$ + $Ca(OH)_2$	0.5 *N* K_2SO_4 + $Ca(OH)_2$	0.5 *N* KCl + KOH
0.0	0.4843	0.4995	0.4966	0.5245	0.4843
1.0	0.5099	0.5118	0.5105	0.5345	0.5119
2.0	0.5247	0.5180	0.5259	0.5527	0.5269
3.0	0.5428	0.5575	0.5475	0.5679	0.5505
4.0	0.6019	0.6125	0.6215	0.6169	0.6136
4.2	0.6187	....	....	....	....
4.4	0.6342	....	....	....	....
4.6	0.6405	....	....	....	....
4.8	0.6651	....	....	....	....
5.0	0.6868	0.6890	0.6894	0.6700	0.6888
5.2	0.6943	....	....	....	....
5.4	0.7059	....	....	...	....
5.6	0.7211	....	....	....	....
5.8	0.7232	....	....	....	....
6.0	0.7387	0.7414	0.7070	0.7330	0.7391
7.0	0.7726	....	....	....	0.7743
8.0	0.7942	....	....	....	....
10.0	0.8529	0.8335	0.7990	0.8443	0.8819

The salt solutions in contact with the soil (Series 0.0 T. $CaCO_3$) in Table III show considerable difference in potential, but all show about the same neutral point, *i. e.*, 5.0 T. $CaCO_3$. From this point the variation in the readings becomes rather wide in both directions.

The general form of the curves is shown by the type curve, Fig. 6. Two points regarding this curve may be discussed. It will be noted that the curve in the slope inclines more toward the vertical as the neutral point is reached and after this point is passed the slope inclines away from the vertical, approaching the slope at the lower end of the curve.

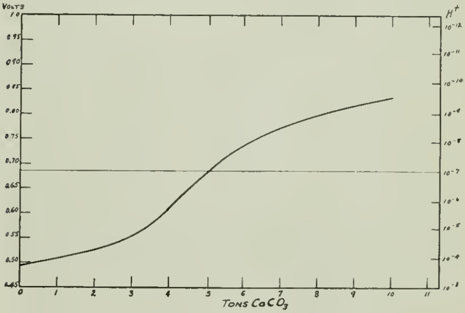

FIG. 6

There is no abrupt change in hydrogen ion concentration, as was noted by Hildebrand,[1] when a strong acid is neutralized by a base, but rather the curve approaches a straight line, *i. e.*, for each addition of base there is a corresponding nearly equal change in hydrogen ion concentration. One may represent the change in the hydrogen ion concentration by the equation

$$\log C = KB + K_1$$

where C is the hydrogen ion concentration, B the base added, and K and K_1 characteristic constants.

The systems investigated above have all the characteristics of mixtures with a high reserve acidity,[2] *i. e.*, the hydrogen ion concentration suffers very little change with comparatively large additions of base. This would be expected if the acid is comparatively insoluble.

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[1] *Loc. cit.*

[2] Washburn. *J. Am Chem. Soc.*, **30** (1908), 37.

Referring again to Table III it will be noted that after the neutral point is reached the hydrogen ion concentration for the system $CaCl_2 + Ca(OH)_2 +$ Soil shows a higher hydrogen concentration than the system KCl + KOH + Soil for the same equivalents of base. This may be accounted for by the precipitating action of calcium hydroxide. The difference in conductivity adds weight to this view.

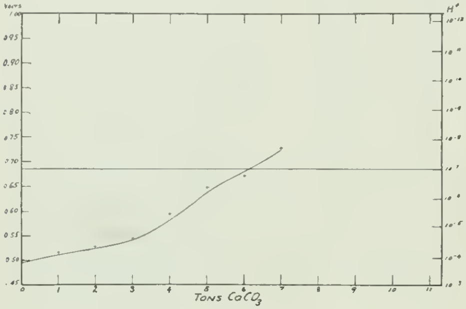

FIG. 7

When the base is allowed to act for a longer period of time there is in general a depression of the whole curve toward the acid side as is shown by Table IV and Fig. 7 which is the graph of the system 0.5 *N* KCl + $Ca(OH)_2$ + Soil.

TABLE IV—EFFECT OF TIME UPON ABSORPTION OF BASE

(Soil used was yellow-gray silt loam. Time, 3 hrs. Results recorded in volts)

T. $CaCO_3$	0.5 *N* KCl + $Ca(OH)_2$	0.5 *N* KCl + KOH
0.0	0.4963	0.4997
1.0	0.5120	0.5157
2.0	0.5249	0.5276
3.0	0.5418	0.5445
4.0	0.5820	0.5959
5.0	0.6397	0.6488
6.0	0.6797	0.6702
7.0	0.7217	0.7268

It will be noted that for the same amount of base there is a higher hydrogen ion concentration than shown in Table III. Hydrogen ion concentration increases with time in the presence of a soluble base.

To compare the change of the hydrogen ion concentration of solutions in contact with different soils, a number of soils were chosen and similar determinations made as with the yellow-gray silt loam in Table IV. All the soils were shaken for 3 hrs. with 50 cc. of 0.5 *N* potassium chloride solution containing the required amount of lime. In each case 5 g. of soil were used, except in the case of the peat soils, of which 2.5 g. were taken. The results are given in Table V.

Graphs of some of the above readings (Fig. 8) show nearly straight line functions. Certain of the soils tested, Nos. 1, 2, 3, 4, 6, and 11, show straight line functions for all measurements taken, while the others show more or less distinct changes in slope at two points, one being on the acid side, *i. e.*, where the H^+ concentration is greater than 10^{-7}, and the other on the basic side. The same is true of the yellow-gray silt loam (Fig. 7). At no point in these graphs is there an abrupt change in slope, as would be expected if we were neutralizing a strong acid, but instead the neutral point is reached at an angle depending upon the character of the soil. It requires comparatively large additions of base to produce a marked change in hydrogen ion concentration.

It may be readily understood that the organic indicators which change color at different hydrogen ion concentrations will show marked differences in the lime requirements of soils, because of the slight change in hydrogen ion concentration with the additions of lime. With the sandy loam soil a change in hydrogen ion concentration of the indicator from 10^{-5} (corresponding to the color change of methyl orange) to 10^{-8} (corresponding to the color change of phenolphthalein) would represent a change in the apparent lime requirement from 0.0 T. to 3 T.; and a change in the lime requirement for peat from about 1 T. to more than 20 T. of calcium carbonate. It is evident that soil solutions may be distinctly acid to litmus while alkaline to methyl orange.

The slight changes in hydrogen ion concentration with addition of base will account for the great variation in results obtained for the lime requirement of soils by the different methods proposed. The greater the slope of the curve the less will be the differences observed. With sandy soils it would be expected that the results obtained by various methods would approach each other, greater variations would be observed with other inorganic soils, while with soils high in organic matter it would be expected that the widest differences would be noted.

The time factor becomes important, as is shown in Tables I and II. The longer the base acts the higher is the hydrogen ion concentration at all initial concentrations of base. The temperature undoubtedly should receive consideration, for the speed of reaction is increased, salts are hydrolyzed to a greater extent,[1] and water of hydration may be decreased with increase in temperature.

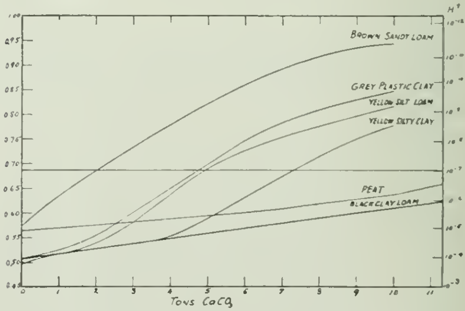

FIG. 8

We should expect that an acid soil would take up larger quantities of calcium from calcium carbonate than from calcium chloride, or sodium from sodium acetate than from sodium chloride as has been repeatedly shown to be the case. This may be explained at least partially by differences in hydrolysis of the salts and the differences in the ionization of the acid.

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[1] Landolt and Börnstein, "Physikalisch Chemische Tabellen."

TABLE V—CHANGE IN HYDROGEN ION CONCENTRATION OF SALT SOLUTIONS IN CONTACT WITH SOILS
(Results recorded in volts)

Ca(OH)$_2$ as T. CaCO$_3$	(1) Black Peaty Loam	(2) Black Clay Loam	(3) Peat	(4) Black Muck	(5) Yellow Silty Clay	(6) Gray Clayey Silt	(7) Gray Plastic Clay	(8) Yellow Plastic Clayey Silt	(9) Grayish Yellow Clayey Silt	(10) Yellow Silt Loam	(11) Brown Sandy Loam
0.0	0.5290	0.5089	0.5654	0.4995	0.4979	0.4707	0.5072	0.4997	0.5034	0.4984	0.5753
1.0	0.5396	0.5171	0.5699	... .	0.5184	0.4831	0.5271	0.5065	0.5126	0.5177	0.6366
2.0	0.5487	0.5257	0.5757	....	0.5199	0.4922	0.5526	......	0.5227	0.5386	0.6887
3.0	0.5629	0.5352	0.5828	....	0.5311	0.5001	0.6077	0.5275	0.5338	0.5780	0.7340
4.0	....	0.5463	0.5705	....	0.5485	0.5076	0.6408	....	0.5538	0.6364	0.7796
5.0	0.5953	0.5571	0.5948	0.5413	0.5942	0.5178	0.6974	0.5719	....	0.6955	0.8240
6.0	....	0.5679	0.6006	....	0.6338	0.5206	0.7485	0.6233	0.6502	0.7297	0.8596
7.0	....	....	....	....	0.6755	....	....	0.6748	....	....	....
8.0	....	....	....	....	0.7164	....	....	0.7216	....	....	....
9.0	....	....	....	....	0.7372	....	....	....	....	....	....
10.0	0.6391	0.6105	0.6373	0.5822	0 7770	0.5820	0.8483	0.7658	0.7737	0.8178	0.9446
15.0	0.6783	0.6470	0.6699	0.6198	....	....	....	....	....	....	....
20.0	0.7267	0.7006	0.7153	0.6684	....	....	....	....	....	....	....

With a carbonate as the reagent, since the point of equilibrium depends also upon the partial pressure of carbon dioxide, it may be understood that the apparent lime requirement may be changed by simply changing the partial pressure of carbon dioxide. The results reported by Ames and Schellenberger,[1] by the Hutchinson-MacLennan[2] and the vacuum methods. are in line with this argument.

The placing of the soil under artificial conditions with respect to temperature, the use of powerful reagents and the extremely finely divided material employed in most of the methods suggested will certainly affect the speed of the reaction. Furthermore, the equilibrium is without doubt a metastable one. The present researches may not be said to be free from these faults.

TABLE VI—CONDUCTIVITY OF SOIL SOLUTION CONTAINING VARIOUS QUANTITIES OF BASE, IN CONTACT WITH ACID SOIL
(Base Calculated as Tons of CaCO$_3$ per Acre
Results = Specific Conductivity × 10^6)

Base Calc. as T. CaCO$_3$	Yellow-Gray Silt Loam. Base Ca(OH)$_2$			Yellow-Gray Silt Loam. Base KOH			Black Peaty Loam Base Ca(OH)$_2$		Black Clay Loam. Base Ca(OH)$_2$
	Standing 1 Hr.	Standing 18 Hrs.	Shaken 3 Hrs.	Standing 1 Hr.	Standing 18 Hrs.	Shaken 3 Hrs.	Standing 1 Hr.	Shaken 3 Hrs.	Standing 1 Hr.
0.0	1.016	1.016	0.913	1.016	1.016	0.913	2.341	2.837	3.813
1.0	1.089	1.129	0.916	1.276	1.203	1.132	2.825	3.388	4.015
2.0	1.220	1.129	0.994	1.733	1.618	...	3.050	3.720	...
3.0	1.638	1.464	1.146	2.520	2.376	1.968	3.468	4.013	4.498
4.0	1.906	1.980	1.495	3.748	3.245	2.402	3.744	4.296	...
4.4	2.033	2.120	1.691	4.637	3.748	...	...	...	...
4.8	2.226	2.248	1.826	5.100	4.122	...	...	...	...
5.2	2.226	2.276	1.980	5.864	4.620	...	...	...	...
5.6	2.346	2.365	2.048	7.318	5.352	...	...	...	...
6.0	2.480	2.352	2.074	9.300	5.978	4.888	4.140	4.767	...
7.0	3.390	2.799	2.310	14.250	8.718	...	4.440	4.968	5.408
10.0	10.170	4.842	3.427	43.580	29.330	25.420	6.055	5.457	5.820

In soils in contact with solutions we have to deal with solid phases whose reaction velocities are necessarily very slow. The substances which produce the acid phenomena when salt solutions are added to acid soils are undoubtedly only slightly soluble and the products formed may pass into similar solid phases. Even substances which are assumed to be soluble may be held in the colloidal condition. Kahlenburg and Lincoln[3] claim that the silicic acid of spring waters is present in the colloidal condition, and the fact that aluminum salts are hydrolyzed to a marked extent while the solubility of aluminum hydroxide is very slight may be taken as an indication that it is held in solution in part as a peptized colloid. The work of Mahin, Ingraham, and Stewart[4] seems to be evidence that the above statement is true in regard to the aluminates.

In anticipation of criticism from the use of neutral salt solution in the potential readings throughout these investigations the following experiment was planned.

It may be reasoned that if slightly soluble acids are present in acid soils it should be possible to measure the hydrogen ion concentration from such a water solution, if the acid ionizes at all, by means of the hydrogen electrode and other indicators. This has been done by Gillespie,[1] but no attempts have been made to follow the change in hydrogen ion concentration upon the addition of a base. In repeating Gillespie's experiment, using yellow-gray silt loam, it was found that after shaking 5 g. of the soil with 50 cc. of distilled water for one-half hour, the potential reading of the mixture was depressed to 0.565 volt, but there is question whether equilibrium had yet been attained considering the fact that neutral salts depress the reading to about 0.5 volt.

The above experiment was modified by using 50 cc. of distilled water containing the equivalent of 4 tons of lime calculated as calcium carbonate. After the readings had become constant 5 g. of yellow-gray silt loam were added and readings taken at stated intervals. The results are given in Table VII.

TABLE VII—CHANGE IN POTENTIAL IN AN ACID SOIL ON SHAKING WITH SOLUTION OF CALCIUM HYDROXIDE

Time Minutes	Volt
0	0.9723
30	0.7056
60	0.6772
90	0.6580
240	0.6529
420	0.6416

Equilibrium evidently had not been reached after 7 hrs. of continuous shaking. In performing the experiment some difficulty was encountered because of the high resistance of the chain, but the readings are typical. It will be noted that the reaction is much slower than in the presence of a neutral salt as may be expected from a consideration of the number of ions present in each case.

The salt solutions used throughout this research, unless otherwise stated, were 0.5 *N*, while the calcium hydroxide solution used above was 0.008 *N*, or an approximate ratio of 500 : 8 at the beginning of the reaction. While the neutral salt concentration remained practically unchanged the calcium hydroxide concentration, and consequently the hydroxyl ion concentration, became progressively less.

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[1] THIS JOURNAL, **8** (1916), 243.

[2] *Chem. News*, **110** (1914), No. 2854, 61.

[3] *J. Phys. Chem.*, **2** (1898), 88.

[4] *J. Am. Chem. Soc.*, **35** (1913), 30.

[1] *Loc. cit.*

The above experiment brings out another fact of importance. After the base has been neutralized the hydrogen ion concentration continues to rise slowly. The substance producing the action comes to an equilibrium very slowly with water, and 6 hrs. after the lime was neutralized hydrogen ions were still being thrown into the solution.

EXPERIMENT IV. CONDUCTIVITY OF SOIL SOLUTIONS—To test the question of the insolubility of the products formed when a base is added to an acid soil, some conductivity experiments were conducted as a preliminary investigation.

Five grams of soil were shaken with 75 cc. of distilled water containing the required amount of base and conductivity measurements made upon the recently shaken mixture of soil and solution with a plunge electrode having a constant of 0.0305. All readings were taken at 25° ± 1°.

From an inspection of Table VI, the following deductions may be made:

The specific conductance increases with each addition of base, but the increase is much greater with potassium hydroxide than with calcium hydroxide. The difference is far too great to be accounted for by the difference in conductivity of potassium and calcium ions.[1] Either the calcium salts formed are less soluble or they must ionize to a far less extent than the potassium salts. The former view is substantiated by the difference noted in the soluble base left in solution when a soil is treated with water containing an excess of base. From the standpoint of the absorption theory it may be argued that calcium hydroxide is absorbed to a greater extent than potassium hydroxide, but this theory can hardly be substantiated in face of the fact that potassium and calcium hydroxide seem to have practically equivalent power to neutralize the acid of the soil noted elsewhere in this paper.

The specific conductivity decreases with time. This is true in every case except with the black peaty loam, where this may be accounted for by the increase in soluble material brought into solution. It will be noted that the conductivity of the water solution in contact with this soil increased after shaking, indicating that equilibrium had not been reached. If this is taken into account, the conductivity of the solution in contact with this loam also decreases with time. It would seem that the reactions are progressive and that equilibrium is not reached for a considerable time period. This is directly in line with the change in hydrogen ion concentration determinations discussed elsewhere in this paper.

As the acid-producing substances present in the soil are extremely insoluble, as shown by the fact that the pure water extract shows little acidity with ordinary indicators, it would be expected that reactions would be exceedingly slow, especially near the equilibrium point. It will be noted in this connection that there was a much more marked change in conductivity with time at the higher concentrations of base.

The rather slow increase in conductivity would point to precipitation effects which are more marked where calcium is used as the base. Acid substances which are highly insoluble would show high reserve acidity, a condition which is quite evident in the soils investigated.

SUMMARY

1—A new hydrogen electrode cell has been designed which has proved satisfactory for certain types of soil investigation.

2—When an acid soil is added to a neutral salt solution the hydrogen ion concentration of the solution reaches a maximum almost immediately if the soil is wet thoroughly by the solution, but secondary reactions later cause a decrease in hydrogen ion concentration of the solution.

3—When an acid soil is added to a neutral salt solution containing a free base the base is neutralized rapidly, as indicated by the change in hydrogen ion concentration of the solution, following closely the law for equilibrium reactions, but the hydrogen ion concentration of the solution continues to rise for an unknown period.

4—There is no sharp break in the progress of base absorption by an acid soil which will warrant any arbitrary division, such as active and latent acidity, or immediate and eventual lime requirement.

5—The changes in log C_H approach nearly straight line functions with progressive addition of base in the presence of a neutral salt solution.

6—Different indicators will give differences in lime requirement for soils depending upon the slope of the log C_H curve. The greatest differences may be expected with soils high in organic matter.

7—A general explanation is given of the different results obtained by different methods for determining soil acidity.

8—When a base is added to an acid soil comparatively insoluble products are formed. Calcium produces a product less soluble than does potassium.

9—The specific conductance of a water solution of an acid soil to which a base has been added increases with each addition of base, but the increase is greater with potassium than with calcium hydroxide, which is far too great to be accounted for by the difference in conductivity of potassium and calcium.

10—Calcium and potassium hydroxide have practically equivalent power to neutralize the acid of an acid soil.

11—The specific conductivity of a pure water solution containing a base in contact with an acid soil decreases with time.

12—An acid soil shows high reserve acidity.

13—The reaction between a water solution of a base and an acid soil is much slower than in the presence of a neutral salt.

14—The absorption of bases by acid soils is due largely to relatively insoluble acids.

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[1] For method of calculating conductance for calcium and sodium ions see Bates, *J. Am. Chem. Soc.*, **35** (1913), 534; and Washburn, "Principles of Physical Chemistry," New York, 1915, p. 214, for calculated values, the equivalent conductance of calcium and potassium ions at infinite dilution being 51 and 63.3, respectively.

THE TRUE TANNING VALUE OF VEGETABLE TANNING MATERIALS[1]

By John Arthur Wilson and Erwin J. Kern

Milwaukee, Wisconsin

Received March 2, 1920

During the past century an enormous amount of energy has been expended in efforts to devise a method for determining the tannin content, or rather the true tanning value, of vegetable materials. Numerous methods have been proposed,[2] but without any indication as to the correctness of the results obtained. In fact the methods now in general use, both here and in Europe, were made official without any knowledge as to their accuracy, but solely because they are of such nature that different analysts have comparatively little difficulty in getting concordant results. Since tanning materials are usually sold on a tannin basis, these methods have proved of very great value in enabling buyer and seller to agree as to price, but investigators who have blindly accepted the results as reliable have sometimes been led into serious error. In this paper we present what we believe to be the first successful method for determining the true tanning value of vegetable materials.

PRACTICAL DEFINITION OF TANNIN

Work on the chemistry of the tannins is still so far from complete that no rigid chemical definition of them as a class can be given, but their extensive use, especially in the leather industry, has necessitated defining them in terms of some property of practical value. It has therefore become customary to apply the name *tannin* to that portion of the water-soluble matter of certain vegetable materials which will precipitate gelatin from solution and which will form compounds with hide fiber which are resistant to washing. The remaining portion of the soluble matter is called *non-tannin*.

NEW METHOD

PRINCIPLE OF THE METHOD—The method aims, of course, to determine exactly what is called for in the definition. A convenient amount of the tanning material is shaken with a definite amount of purified hide powder until all tannin has been removed from solution. This point is determined by filtering off a portion of the residual liquor and adding drop by drop, avoiding a large excess, a solution containing 10 g. of gelatin and 100 g. of sodium chloride per liter; if the solution becomes turbid or a precipitate forms, it shows that all tannin has not been removed from solution, in which case the mixture must be discarded and the test repeated, using less of the tanning material or shaking for a longer time, until the solution after filtration gives no visible reaction with the gelatin-salt reagent. The tanned powder is then washed free from soluble matter, including the non-tannin removed from solution by the hide powder, which is responsible for the large errors in the methods now in use. It is then carefully dried and analyzed for tannin as in the regular procedure for vegetable-tanned leathers, and from this figure the percentage of tannin in the original material may readily be calculated.

SENSITIVITY OF GELATIN-SALT TEST AND ITS EFFECT UPON THE METHOD—The gelatin-salt test appears to be the most satisfactory one known for determining whether or not a tan liquor has been completely detannized. In the present official methods, it is assumed that the hide powder completely detannizes the liquor because the non-tannin filtrate remains clear upon addition of the gelatin-salt reagent. This reagent, however, gives negative results with extremely dilute solutions of tannin. Another fact tending to make it difficult to detect the presence of small amounts of free tannin in the liquor after shaking with hide powder is that these liquors are always turbid and must be filtered, and it is a known fact that filter paper will remove tannin from solution to some extent. It was therefore essential to determine the sensitivity of the test for the conditions under which the analyses were made.

If the time of shaking, volume of tan liquor, and quantity of hide powder are kept constant, the less the concentration of the liquor the greater will be the fraction of tannin removed by the hide powder. This made it desirable in checking the accuracy of the work to make several sets of analyses for each tanning material examined, using a different concentration of liquor in each case. The most concentrated solution of each material noted in Table I was used to test the sensitivity of the gelatin-salt reagent by diluting to greater and greater extent and *then* filtering and testing with the reagent under the same conditions as employed in the actual analyses. The reagent was added a drop at a time to 10 cc. of the clear filtrate in a test-tube. The dilutions at which the test failed, expressed in cc. of tan liquor diluted to 100 cc., were as follows: quebracho 1, hemlock bark 2, oak bark 2, larch bark 2, chestnut wood 0.5, osage orange 2, sumac 1, and gambier 4. It therefore follows, since the detannized filtrates from all these liquors gave a negative test with the gelatin-salt reagent, that more than 95 per cent of the tannin of the gambier liquor and more than 97 per cent of the tannin of every other liquor were removed from solution by the hide powder. But the analyses were also carried out with much more dilute liquors, from which the hide powder should remove an even greater percentage of the tannin. Since the results obtained for any one material, using several dilutions, checked so closely, we may reasonably conclude that the hide powder removed *practically* all of the tannin from all solutions which gave no test with the gelatin-salt reagent after the shaking process.

HIDE POWDER—The hide powder used in this work is a highly purified product known as American Standard and is prepared by the Standard Mfg. Co. of Ridgway, Pa., especially for use in the analysis of tanning materials. Since this hide powder is of variable composition due to changes in water content, it was necessary to base our calculations upon the protein it contained, to which we shall hereafter refer simply as hide substance. Von Schroeder[1] found hide substance to contain 17.8 per cent of nitrogen, which figure is generally accepted. The per cent of nitrogen determined by the Kjeldahl method, multiplied by 5.62, should therefore give the per cent of hide substance. The hide powder used in this work showed by analysis

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[1] Presented before the Section of Leather Chemistry at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 14, 1920

[2] For a review of work done since 1803, see Procter's "Leather Industries' Laboratory Book" (Spon, 1908), pp. 168–176.

[1] Procter, *Loc. cit.*

	Per cent
Water	12.29
Ash	0.36
Fat (chloroform extract)	0.82
Hide substance (N × 5.62)	86.50
TOTAL	99.97

from which it would appear that the factor 5.62 is correct.

MATERIALS EXAMINED—Eight materials were selected for examination which are fairly extensively used and which show great differences in properties, especially in so-called astringency. The solid quebracho extract and the four liquid extracts of oak bark, larch bark, chestnut wood, and osage orange are typical samples of the best of these materials now on the American market. The gambier is the ordinary pasty product from the East Indies; the sumac, consisting of ground leaves and small twigs, is from a reputable dealer in Palermo; and the hemlock bark came from the forests of Wisconsin.

PROCEDURE—The extracts were simply dissolved in hot water, cooled slowly, and made up to the mark. The bark and sumac were finely ground and leached by percolation, only the extracted portions being used after making up to definite volume. In each test, 12 g. of hide powder (of known hide substance content) were put into a wide-mouth, rubber-stoppered, half-pint bottle, the tanning material dissolved in 200 cc. of solution was added, and the whole was shaken in a rotating box for 6 hrs.

The amount of material that could be used was limited by the amount of tannin that the hide powder was capable of taking up in 6 hrs. On the other hand it was desirable not to use too little, since the less the amount of tannin fixed per unit of hide substance, the less the accuracy of the method, since the tannin was determined by difference. Whenever the liquor after the 6-hr. shaking gave a turbidity or precipitate with the gelatin-salt reagent, the test was repeated with less material. The smallest amount used for any material represents the least we were able to use and still get reproducible results.

The tanned powder was washed by shaking with 200 cc. of water for 30 min., squeezing through a suitable cloth, and repeating the washing operation until the wash water showed no color and gave no test with ferric chloride solution. Except for the osage orange and chestnut wood extracts, which are unusual in several respects, not more than 12 washings were required to free the powders from non-tannin, which shows that the line of demarcation between tannin and non-tannin is fairly sharp for the commoner materials. The wash water continued to extract coloring matter from the powders tanned with osage orange until after the fiftieth washing, while as many as 25 washings were required to free the powders tanned with chestnut wood from soluble matter producing a dark color with ferric chloride. All wash water was tested with the gelatin-salt reagent, but in every case the test was negative. This method of washing was found to be more efficient than using running water on a suction filter, probably because the mechanical agitation assists the diffusion of soluble matter from the interior of the hide fibers.

The washed powders were dried at room temperature for 24 hrs. or longer and then analyzed for water, ash, fat, and hide substance. The difference between 100 and the sum of these percentages was taken as the per cent of tannin in the leather. The parts of tannin per 100 parts of hide substance in the leather divided by parts of tanning material used per 100 parts of hide substance gave the fraction of tannin in the original material.

The results for the eight materials examined are given in Table I.

TABLE I

MATERIAL	Material Grams per Liter	Percentage Analysis of Tanned Hide Powder					Per 100 G. of Hide Substance		Tannin in Material Per Cent
		Water	Ash	Fat	Hide Substance (N × 5.62)	Tannin (by Difference)	Tannin Found Grams	Material Used Grams	
Quebracho	18.8	11.56	0.14	0.35	74.92	13.03	17.39	36.8	47.26
Quebracho	18.8	11.42	0.08	0.35	75.05	13.10	17.46	36.8	47.45
Quebracho	11.5	13.81	0.03	0.30	77.53	8.33	10.74	22.6	47.52
Hemlock Bark	150.0	9.94	0.12	0.24	76.54	13.16	17.19	287.9	5.97
Hemlock Bark	100.0	10.73	0.13	0.28	79.39	9.47	11.93	191.9	6.22
Hemlock Bark	75.0	12.76	0.05	0.28	79.53	7.38	9.28	147.1	6.31
Oak Bark	67.5	12.54	0.07	0.12	74.76	12.51	16.73	131.6	12.71
Oak Bark	45.0	11.19	0.09	0.24	79.36	9.12	11.49	87.6	13.12
Oak Bark	25.0	13.53	0.05	0.34	81.00	5.08	6.27	48.9	12.82
Larch Bark	67.5	12.59	0.09	0.13	75.61	11.58	15.32	131.6	11.64
Larch Bark	45.0	13.65	0.09	0.30	77.90	8.06	10.35	87.7	11.80
Larch Bark	25.0	16.52	0.08	0.25	78.65	4.50	5.72	48.9	11.70
Chestnut Wood	67.5	12.43	0.11	0.05	75.76	11.65	15.38	131.6	11.69
Chestnut Wood	45.0	12.82	0.13	0.19	78.54	8.32	10.59	87.7	12.08
Chestnut Wood	37.5	12.05	0.10	0.21	80.74	6.90	8.55	71.7	11.92
Sumac	93.8	11.39	0.16	0.36	74.92	13.17	17.58	179.3	9.80
Sumac	62.5	12.26	0.23	0.31	78.38	8.82	11.25	119.5	9.41
Sumac	37.5	11.75	0.12	0.37	81.97	5.79	7.06	73.5	9.61
Osage Orange	48.8	12.82	0.13	0.17	77.35	9.53	12.32	95.0	12.97
Osage Orange	32.5	12.83	0.09	0.25	80.09	6.74	8.42	63.3	13.30
Osage Orange	26.3	12.43	0.12	0.25	81.43	5.77	7.09	51.2	13.85
Gambier	50.0	12.08	0.18	0.19	81.44	6.11	7.50	97.4	7.70
Gambier	49.5	11.77	0.26	0.28	81.70	5.99	7.33	94.7	7.74
Gambier	29.0	13.06	0.14	0.35	82.74	3.71	4.48	56.5	7.93

COMPARISON WITH A. L. C. A. METHOD

Practically all tanning materials are bought and sold in this country on the basis of tannin content as determined by the official method of the American Leather Chemists Association. The principle of the method is similar to that of the new method as regards the shaking of a solution of the tanning material with hide powder, but differs in that the drop in concentration of the liquor upon shaking is taken as the measure of its tannin content, while the tanned powder is simply discarded. The details of the A. L. C. A.[1] method follow:

> The hide powder is specially prepared by giving it a light chrome tannage with chrome alum, washing it practically free from soluble matter, and squeezing it until it contains not less than 71 nor more than 74 per cent of water. The solution of tanning material for analysis must contain not less than 0.375 nor more than 0.425 g. of tannin per 100 cc., as found by this method. To 200 cc. of this solution is added such an amount of the wet hide powder as contains not less than 12.2 nor more than 12.8 g. of dry hide powder and the whole is shaken for 10 min. The limits defined are to some extent arbitrary, but it has been found necessary to set limits of some sort in order to get concordant results. The detannized solution is separated from the powder by squeezing through linen and is then filtered through

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[1] *J. Am. Leather Chem. Assoc.*, **14** (1919), 654.

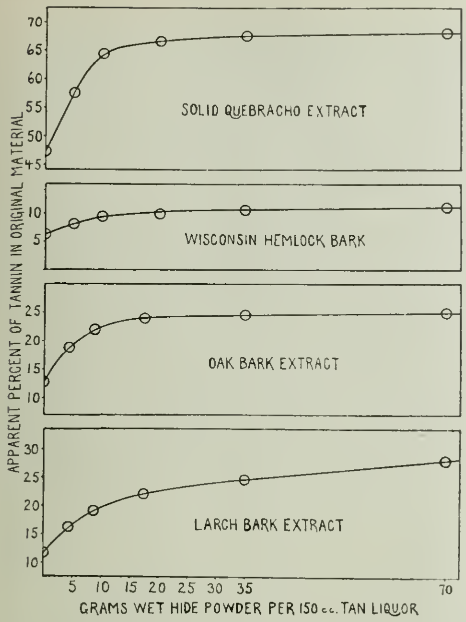

Fig. 1

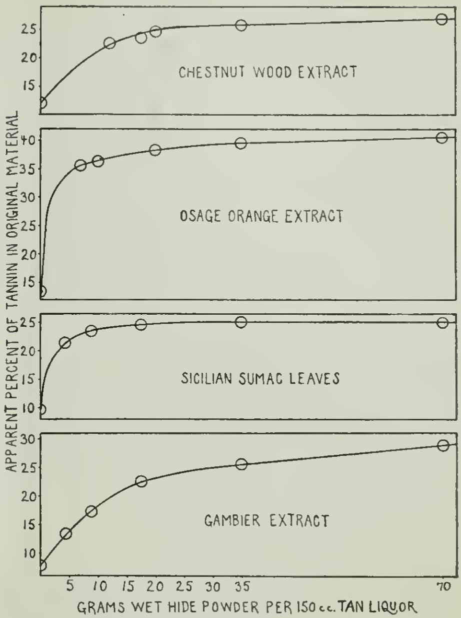

Fig. 1*a*

paper, after the addition of kaolin, the solution being returned until the filtrate is quite clear. The amount of residue from an aliquot portion of this filtrate, after correcting for the water introduced by the hide powder, is taken as a measure of the non-tannin in the original material. The difference between the total soluble matter and the non-tannin is called tannin.

Several outstanding sources of error in this method were emphasized by the authors in an earlier paper.[1] The most serious defect is that it does not take into account the fact that hide powder removes non-tannin of certain kinds, such as gallic acid, pyrocatechol, etc., from solution to an extent depending upon the concentration. These substances do not make leather and are readily washed out. This explains the fact that where tanners try to keep a rigid cost account of tanning materials, they find no such amount of tannin in the leather as would be expected from the amount of tannin used, as determined by the A. L. C. A. method. The analyses of the eight materials by the A. L. C. A. method are given in Table II along with a calculation of the percentage errors involved in this method, made upon the assumption that the results obtained by the new method are correct.

Table II

	Percentage Analysis of Material					
	A. L. C. A. Method					
			Soluble Matter			
Material	Water	Insoluble Matter	Non-tannin	Tannin	New Method Tannin	Percentage Error in A. L. C. A. Method
Quebracho	17.87	7.16	6.96	68.01	47.41	43
Hemlock Bark	8.90	74.33	6.71	10.06	6.17	63
Oak Bark	52.66	3.68	19.46	24.20	12.88	88
Larch Bark	51.08	5.88	20.90	22.14	11.71	89
Chestnut Wood	58.90	1.50	13.80	25.80	11.90	117
Sumac	9.25	47.20	17.99	25.56	9.61	166
Osage Orange	46.05	3.45	10.63	39.87	13.37	198
Gambier	51.12	5.36	18.57	24.95	7.79	220

Although the enormous errors in the A. L. C. A. method are nothing short of sensational, we are convinced that they are not at all exaggerated. The extent of these errors is less surprising, however, when the behavior of certain non-tannins, like gallic acid, in the presence of hide powder is studied. A series of solutions of gallic acid of different strengths was prepared and treated by the A. L. C. A. method as though they were tan liquors of the required strength. The results for non-tannin should have been 100 per cent in every case, if the method were reliable, but the actual data in Table III show that a very large proportion of the acid is taken up by the hide powder.

Table III—Results of Treatment of Pure Gallic Acid Solutions by the A. L. C. A. Method

Using 47 g. of wet hide powder (73% water) to 200 cc. of solution

Gallic Acid Grams per Liter	Non-tannin Per cent	Tannin Per cent
8.88	54.0	46.0
4.44	47.1	52.9
2.22	43.8	56.2
1.11	40.4	59.6

Table IV—Effect of Altering Proportion of Hide Powder upon Amount of Gallic Acid Removed from a 0.888 Per cent Solution

Using the principle of the A. L. C. A. method

Wet Hide Powder (73% water) G. per 200 cc.	Non-tannin Per cent	Tannin Per cent
5	91.8	8.2
10	86.0	14.0
25	69.6	30.4
50	52.1	47.9
75	43.7	56.3

Table IV shows that the amount of gallic acid removed from solution is very largely dependent upon the proportion of hide powder employed. Our results by the new method for gambier indicate that this sample contains more than 4 times as much non-tannin as tannin. When we consider that more than 50 per cent of these non-tannins may be removed from solution by the hide powder, errors exceeding 200 per cent are to be expected by the A. L. C. A. method.

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[1] *J. Am. Leather Chem. Assoc.*, 13 (1918), 429.

The reason for the necessity of arbitrary limits in the official method is suggested by the gallic acid experiments, but is more strongly emphasized by similar experiments upon actual tan liquors. The effect of altering the proportion of hide powder with solutions of the eight tanning materials is shown in Table V and Figs. 1 and 1*a*. The zero points in the figure represent the percentages of tannin found by the new method. In none of these experiments did the solution after shaking give a test with the gelatin-salt reagent, but we nevertheless find enormous increases in per cent of tannin due to increasing the proportion of hide powder. This alone should be sufficient to show that the A. L. C. A. method cannot be considered an exact one and that the arbitrary limits were set so that different analysts would get concordant rather than more nearly correct results. Table V and Fig. 2 show how the percentage error increases with increasing proportions of hide powder.

Table V

Material	Grams per Liter	Wet Hide Powder (73% Water) Used to Detannize 150 Cc. Tan Liquor Grams	Apparent Per cent of Tannin	Percentage Error Due to Hide Powder
Quebracho	3	70.0	68.18	44
		35.0	67.56	43
		20.0	66.61	40
		10.0	64.36	36
		5.0	57.56	21
Hemlock Bark	20	70.0	10.98	78
		35.0	10.60	72
		20.0	9.76	58
		10.0	9.35	52
		5.0	7.98	29
Oak Bark	4.11	70.0	25.02	94
		35.0	24.59	91
		17.5	24.01	86
		8.8	22.09	72
		4.4	18.77	46
Larch Bark	4.37	70.0	28.10	140
		35.0	24.52	109
		17.5	21.97	88
		8.8	19.10	63
		4.4	16.24	39
Chestnut Wood	15	70.0	26.87	126
		35.0	25.80	117
		20.0	24.59	107
		17.5	23.52	98
		12.0	22.49	89
Sumac	4	70.0	24.98	160
		35.0	25.05	161
		17.5	24.47	155
		8.8	23.45	144
		4.4	21.45	123
Osage Orange	8	70.0	40.48	203
		35.0	39.47	195
		20.0	38.21	186
		10.0	36.27	171
		7.0	35.67	167
Gambier	4.58	70.0	29.04	273
		35.0	25.60	229
		17.5	22.56	190
		8.8	17.22	121
		4.4	13.38	72

As might be expected, the greatest errors in the Official method are obtained with those materials containing the greatest proportion of non-tannin to tannin. Quebracho, having least non-tannin, gives the smallest error. However, if the quebracho is mixed with gallic acid to make the proportion of non-tannin to tannin about the same as in the case of the gambier, it gives errors nearly as great as in the case of the gambier. This is shown in Table VI.

Table VI

Wet Hide Powder (73% Water) Used to Detannize 150 Cc. Tan Liquor Grams	Percentage Analysis of Mixture of 5 Parts of Quebracho Extract to 9 Parts of Dry Gallic Acid: A. L. C. A. Method: Water	A. L. C. A. Method: Insoluble Matter	A. L. C. A. Method: Soluble Matter: Non-tannin	A. L. C. A. Method: Soluble Matter: Tannin	New Method Tannin	Percentage Error Due to Hide Powder: Quebracho: Alone (from Fig. II)	Quebracho: In Presence of Gallic Acid	Gambier (from Table V)
4.4	5.80	3.96	63.34	26.90	16.93	18	59	72
8.8	5.80	3.96	53.39	36.85	16.93	33	118	121
17.5	5.80	3.96	44.07	46.17	16.93	39	173	190
35.0	5.80	3.96	37.14	53.10	16.93	43	214	229
70.0	5.80	3.96	33.87	56.37	16.93	44	233	273

Comparison of the two methods has brought out at least one fact of practical significance: Those materials which give the least errors are most astringent, while those giving greatest errors are least astringent. The order of the materials in Table II might almost be taken as the order of decreasing astringency, although an exact parallelism cannot be claimed since we have no quantitative measure of astringency. Quebracho and hemlock bark are generally conceded to be the most astringent, and sumac and gambier the least astringent of these materials. This suggested a relation between astringency and the ratio of non-tannin to tannin. In the experiments listed in Table I, the hide powder fixed more than twice as much tannin from the quebracho liquors in 3 hrs. as from the gambier liquors in 6 hrs. But, when enough gallic acid was added to the stronger quebracho liquors to give them the same proportion of non-tannin to tannin as in the gambier, the hide powder did not remove anywhere nearly all the tannin in 6 hrs. Upon addition of the gelatin-salt reagent to the liquors after shaking, huge precipitates were formed, suggesting a great reduction in astringency. That the effect was only one of slowing up the tanning action was proved by the fact that the hide powder was able to detannize the solution completely in 24 hrs.

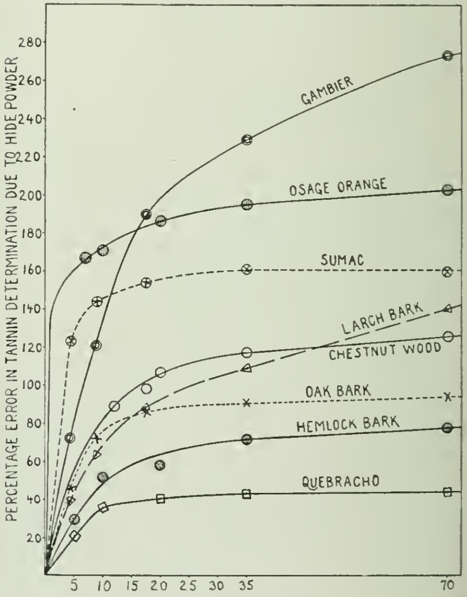

Fig. 2

PRACTICABILITY OF THE NEW METHOD

The new method in its present form requires more time than the A. L. C. A. method, but this disadvantage must be considered negligible compared to the advantage of greatly increased accuracy. If the new method is to prove satisfactory from the standpoint of setting a price on tanning materials, it must give results which are readily reproducible in different laboratories. We are convinced that it will do this quite as well as the official method when the different analysts become used to manipulating it. The several results for any one material in Table I were determined days, and sometimes weeks, apart. The hide powder used in the new method is not chromed, but is used exactly as it comes from the manufacturer. If, however, it is first chromed, it gives a higher result for osage orange, apparently due to the chrome acting as a mordant for the coloring matter. But this coloring matter does not precipitate gelatin nor does it form a stable compound with unchromed hide fiber and we feel that the method is the more accurate for not estimating this coloring matter as tannin. The question of putting a value on this coloring matter may have to be solved, but this problem will probably be confined to very few materials. On the whole we believe the new method will be found quite as practicable and certainly very much more satisfactory from the standpoint of accuracy than the present official method. What has been said concerning the A. L. C. A. method applies equally well to the European methods since they differ only in detail.

SUMMARY

A new method of tannin analysis is described which we believe determines exactly what is called for in the generally accepted definition of tannin from a practical viewpoint, namely, that portion of the water-soluble matter of certain vegetable materials which will precipitate gelatin from solution and which will form compounds with hide fiber which are resistant to washing.

The analyses of eight common tanning materials by the new method and by the official method of the American Leather Chemists Association indicate that the latter method is in error to the extent of from 43 to 220 per cent.

The new method gives reproducible results and is considered entirely practicable.

PRACTICAL METHODS FOR THE DETERMINATION OF RADIUM. III—ALPHA-RAY METHOD, GAMMA-RAY METHOD, MISCELLANEOUS[1]

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Received October 29, 1919

In two previous papers[2] the writer has described a form of interchangeable electroscope, the details of its construction, and its use in connection with the determination of radium by the emanation method. In the present paper, it is proposed, first, to discuss briefly some more recent modifications in the construction of the electroscope, which have contributed materially to the ease and accuracy of its manipulation; second, to discuss rather fully the application of the α-ray method to the determination of radium in solids without reference to any particular form of electroscope; and, third, to consider briefly the γ-ray method of determining radium.

MODIFICATIONS IN THE INTERCHANGEABLE ELECTROSCOPE

Conditions due to the European war necessitated an electroscope of American make. In devising one, the writer had economy and accuracy equally in mind, and sought to combine as far as possible in a single instrument the advantages of the various types already in use. The advantages sought have already been mentioned,[1] but perhaps a somewhat fuller explanation in the way of acknowledgments will not be out of place. The "interchangeable" feature, enabling the use of a detachable head carrying the reading device and leaf system, was first used by Professor Ebler,[2] in connection, however, with the Exner type of double-leaf electroscope. Instead of the latter, it was desirable to use the simpler single-leaf Wilson type so modified that the leaf could be readily removed if replacements were necessary.

The highly advantageous feature of having the reading microscope firmly fixed to the head so there can be no chance of accidentally changing the relative positions of leaf and micrometer scale of the microscope was adapted from the Wulf[3] electrometer, thus providing rigidity while preserving complete visibility of the leaf system—an advantage not possessed by the Wulf instrument.

The most far-reaching change in the instrument, since its earlier description, consists in the substitution of amber or amberoid insulation instead of sealing-wax for both insulators (points g and d in the original).[4] This substitution made it necessary, however, to provide a new means of rendering the emanation chamber gastight. This has been accomplished without the use of any binding material by an ingenious arrangement, due to Mr. P. F. Elzi, of the Sachs-Lawlor Company, Denver. Fig. 1 illustrates its construction. The brass collar a is threaded into the lower chamber (not shown) at b and made gastight by means of a lead washer, c. The collar a is hollow and provided with an interior projecting shoulder, d, on which rubber washers rest at f and f' above and below. On f and f' rest amberoid discs, g and g', pierced by the rods h and h', both of which are threaded into the connector i. The holes through g and g' are made tight by small rubber washers j and j'. h terminates above in a shoulder, k, resting on the washer j and a tip l to make electrical contact with the spring s attached to the leaf system above. Below, h' is provided with a similar shoulder, k', which rests on the washer j' and leads below to the electrode e. By screwing h and h' into the common connector i, tension is applied on the washers f and f' and j and j', thus giving gastightness to the lower chamber without any binding material. This simple device has proved eminently satisfactory, usually holds gastight for a year or more, and can be readily tightened or, if necessary, taken apart to renew the washers. Much labor in recalibrating the instrument is avoided in this way.

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[1] Published with permission of the Director of the U. S. Bureau of Mines.

[2] This Journal, 7 (1915), 406, 1024.

[1] Part I, *Loc. cit.*

[2] *Chem. Kalendar*, **1914**, Part II, 367.

[3] *Physik Z.*, **8** (1907), 246, 527.

[4] Part I, *Loc cit* Fig 3

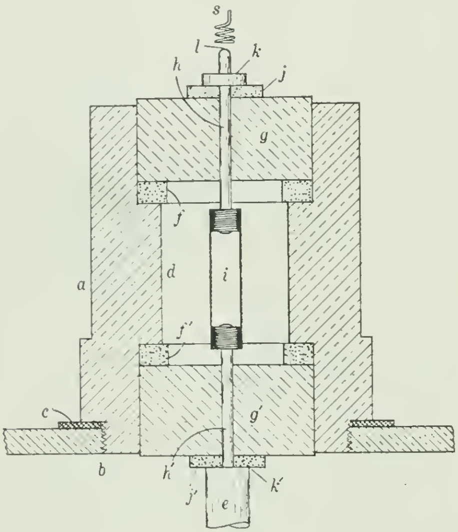

FIG. 1—COLLAR OF ELECTROSCOPE WITH AMBEROID INSULATORS MADE GASTIGHT WITHOUT CEMENT

Further changes have consisted in replacing the two rubber-connected glass stopcocks with metal stopcocks brazed into the chamber. The microscope holder has also been made adjustable by means of a heavy milled-head screw (Fig. 2). In the new construction the front metal plate carrying the microscope fits into the head cylinder by means of a V-groove carrying three tightening screws, by loosening which the plate can be rotated to bring the microscope to view the leaf at any desired part of its arc.

The changes mentioned above have materially added to the usefulness and accuracy of the interchangeable electroscope.

THE ALPHA-RAY METHOD OF ESTIMATING RADIUM IN SOLIDS

In its simplest form, this method consists in exposing a solid powder covering a plate of definite surface and depth in the discharge chamber of an electroscope, which might be of the type illustrated by the middle chamber shown in Fig. 2. By comparing the rates of discharge of the leaf as viewed through a microscope provided with a micrometer scale, first using a solid with known uranium or radium content and later the unknown, a more or less approximate idea is obtained of the radium or uranium content of the latter.

This method, as practically applied to radioactive ores, has been described by Moore and Kithil[1] and briefly commented on by Parsons, Moore, Lind, and Schaefer.[2] Its refinement for scientific measurements, with reference to the penetration of layers of various depths by α-rays, has been carefully worked out by McCoy.[3] Owing to its sensitiveness, simplicity, and ease of manipulation, this method has been more generally used than any of the methods of measuring radioactivity. α-Ray instruments are now very generally used in prospecting, ore sorting and milling, and for certain purposes even in the control of radium plant operations. For qualitative and very roughly quantitative purposes the α-activity furnishes a quick and satisfactory method. Attempts to extend its use for more quantitative purposes are beset with many pitfalls and uncertainties which are discussed in this paper. To illustrate the fundamental difficulty in its use for quantitative purposes, complaint has been made that the results of α-ray activity measurements frequently do not check even roughly with other results, such as the determination of uranium by chemical methods, or the direct determination of radium by the emanation method. These discrepancies have been especially marked for carnotite ores from different localities, as can be seen from Table I.

TABLE I—SHOWING THE VARIABILITY OF DIFFERENT CARNOTITES IN α-RAY ACTIVITY PER URANIUM CONTENT

SAMPLE	Per cent U_3O_8 (By Analysis)	α-Activity (Arbitrary Units)	$\frac{\alpha\text{-Activity}}{\text{Per cent } U_3O_8}$	Em. power Per cent	$\frac{Ra}{U}$	$\frac{\alpha\text{-Activity}}{\text{Per cent } U_3O_8}$ Corrected
1...	1.52	0.087	0.0572	20.4	102.7	0.0638
2...	1.60	0.064	0.0400	50.5	94.9	0.0582
3...	2.07	0.139	0.0671	29.6	101.5	0.0804
4...	3.16	0.172	0.0544	39.7	119.2	0.0631
5...	4.78	0.207	0.0433	33.90	98.8	0.0542
6...	9.12	0.259	0.0284	30.4	84.1	0.0382
7...	23.40	0.733	0.0313	45.8	72.4	0.0508
8...	33.20	1.206	0.0363	16.2	107.8	0.0381

In Table I, the samples of carnotite represent all grades from a low to a high percentage of U_3O_8, and also come from various localities in Colorado and Utah.

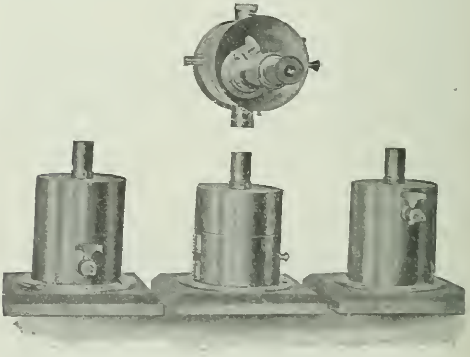

FIG 2

If the α-ray method, as usually applied, were really applicable to all carnotites, then the ratio of surface activity to the percentage of U_3O_8 given in the fourth column should be constant. Evidently this is not even approximately true, and one can see at once how far astray one might be led in choosing any of these different samples as standards for other α-ray comparisons.

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[1] U. S. Bureau of Mines, *Bulletin* **70** (1913), 64.

[2] *Ibid.*, **104** (1916), 87.

[3] *Phys. Rev.*, **1** (1913), 393.

In seeking the reason for these deviations, three principal causes present themselves:

1—Variation in the amount of the loss of radium emanation by gaseous diffusion from the ore; the percentage loss is usually referred to as the "emanating power." This entails the loss of α-radiation, not only from the emanation itself, but also from the succeeding α-ray members, RaA, C, and F. The actual percentage loss for the ores under consideration is reported in the fifth column of Table I, and, as has already been pointed out by Lind and Whittemore,[1] is not only unusually high for carnotite, but also quite variable.

2—A second possible source of error is the variability of the radium-uranium ratio in carnotite. As also reported by Lind and Whittemore,[2] this variation is confined to *small* specimens of carnotite which can vary considerably from the normal value of the radium-uranium ratio. This variation is reported in the sixth column of Table I in terms of per cent, placing the normal (pitchblende) ratio equal to 100 per cent. In the last column the values of Column 4 have been corrected according to the data in Columns 5 and 6; that is, the discrepancies introduced by the variation of α-radiation, due to "emanating power" and abnormal ratio of radium to uranium, have been eliminated. The improvement in the degree of constancy of activity compared with the uranium content can be seen to be very slight. Evidently there must be another source of error more far-reaching in its influence than either of the first two.

3—This source of error lies in the position of the radioactive material in the individual grains and also to some extent in the nature of the gangue material. Since the α-ray can penetrate material of the density of silica very slightly—only about 0.03 mm., or 0.001 in.—it is evident that the effective rays come only from near the surface, and any variation of the position of the active material in different samples with respect to the surface would have a great influence on the α-ray activity observed. It is also evident that fine grinding would not obviate the difficulty materially, as it would be impossible to produce comminution below 0.001 inch. McCoy's method of correcting for the absorption could be applied, but is hardly within the powers of the ordinary operator, does not obviate the difficulties due to 1 and 2, and involves time and labor to a prohibitive degree for ordinary practical purposes. In short, any efforts to make the α-ray method really accurate involve more labor than a direct radium determination by the emanation method. There is one favorable factor, however, to the advantage of the α-ray comparison, even for carnotite, namely, that specimens from the same mine or claim do not usually show such wide deviation in the ratio $\frac{\text{activity}}{\text{per cent } U_3O_8}$ as those reported in Table I.

With reference to carnotite in general, the conclusion must be drawn that the α-ray method can by no means take the place of a direct radium determination, nor of a uranium analysis, for purposes of sale or for scientific or commercial control. Qualitative and very roughly quantitative results only can be expected. It is not desired that the foregoing shall discourage the use of the α-ray method. Its application is so simple and its results so quickly derived that it will continue to be of great service in obtaining preliminary estimates of the content of radioactive materials as well as invaluable in their detection. It is merely meant to emphasize that it cannot be relied on for final quantitative measurements.

PITCHBLENDE—With reference to pitchblende, the case is decidedly more favorable for the use of the α-ray method. Since the emanation loss is small and varies only slightly in pitchblende, the first difficulty is practically eliminated. The radium-uranium ratio also appears to be constant for all different samples of pitchblende,[1] which eliminates the second difficulty. From the results reported in Table II, the third difficulty also appears to be slight, perhaps due to the primary nature of pitchblende as compared with carnotite, a secondary mineral. At any rate, pitchblendes of different grades can be compared with a fair degree of accuracy.

TABLE II—SHOWING THE RELATIVE CONSTANCY OF THE RATIO $\frac{\text{PER CENT } U_3O_8}{\alpha\text{-ACTIVITY}}$ IN PITCHBLENDES

SAMPLE	Per cent U_3O_8 (By Analysis)	α-Activity (Arbitrary Units)	$\frac{\text{Per cent } U_3O_8}{\alpha\text{-Activity}}$
1	4.15	0.150	27.7
2	8.02	0.296	27.0
3	10.55	0.388	29.2
4	16.4	0.576	28.5
5	17.3	0.572	30.2
6	24.7	0.931	26.6
7	25.3	0.973	26.0

While it would hardly be advisable to use the method where great accuracy is desired, for many purposes it can be employed with convenience and satisfaction.

SULFATES—One of the intermediate products in the production of radium by most of the different processes consists in a precipitated $(Ra)BaSO_4$. The writer has found by experience that if the radium content is not too high to preclude the possibility of using the α-ray method, the results approximate fairly closely to the radium content, as may be seen from Table III.

TABLE III—SHOWING THE APPROXIMATE CONSTANCY OF $\frac{\text{RADIUM}}{\alpha\text{-ACTIVITY}}$ IN CRUDE $(Ra)BaSO_4$

SAMPLE	Mg. Ra per Kilo (Emanation Method)	α-Activity (Arbitrary Units)	$\frac{\text{Radium}}{\alpha\text{-Activity}}$
P_1	1.41	0.71	1.98
P_3	2.15	1.20	1.79
40	1.32	0.73	1.80
70	2.18	1.28	1.70

While the results for the sulfates are not so good as with pitchblende, they show that for a quick measurement preliminary to the employment of the emanation method the α-ray method may be used with benefit. The α-ray method has also been used very successfully in the determination of other radioactive substances in small quantity for scientific purposes; but since it is the object of the present paper to deal only with the practical methods of measuring radium itself, they do not require consideration here.

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[1] *J. Am. Chem. Soc.*, **36** (1914), 2066.

[2] *Loc. cit.*

[1] Heimann and Marckwald, *Jahrb. Radioakt. Elektronik.*, **10** (1913), 299.

THE GAMMA-RAY METHOD OF MEASURING RADIUM

Radium itself emits α-rays only, but both RaB and RaC emit γ-rays which present the most convenient means of measuring radium in quantities above 0.1 mg. and of not less than 0.05 per cent purity. Since RaB and RaC are products resulting from the decay of radium emanation, a gas, it is necessary to confine radium preparations in a closed vessel to prevent the escape of gas before the measurement is made. The measurement may be carried out after the vessel has been closed for a month or more, in which case the γ-radiation will have reached a constant maximum and no time correction will be necessary; the γ-radiation then having become directly proportional to the quantity of radium present, as is the case of all standard tubes of radium salt which have been sealed for more than a month. If the measurement is made prior to this period, a correction must be made for the unelapsed time. This correction is readily made by reference to the Kolowrat table, just as described in Part II[1] for the emanation method.

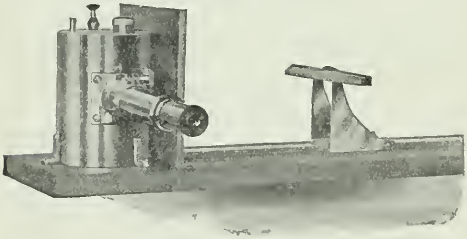

FIG. 3

In order that the accumulation of emanation shall have taken place over a definite period of time, the starting point must be rendered exact by sealing the radium salt in a glass tube as soon after crystallization as possible. It is first necessary, however, to dry the salt thoroughly by raising the temperature for 20 min. or more to 250° C. or higher. Otherwise, decomposition by the α-rays of any water remaining, even in the form of water of crystallization, would generate a dangerous gas pressure in the limited volume of the tube. If the zero period is indefinite or not known, a series of measurements must be made at different intervals, from which the final maximum value can be calculated by comparisons with the Kolowrat table.

The measurement itself consists simply of a comparison of the rates of discharge produced by a tube with known radium content and that of the unknown, each being placed successively in the same fixed position at a suitable distance from the discharge chamber. Almost any type of electroscope may be used by placing a lead screen, one-eighth to one-fourth inch thick, between the instrument and the tube containing the radium. A type of γ-ray electroscope is shown in Fig. 3.

An accuracy of about 1 per cent can be readily attained with ordinary precautions by the use of the simple aluminum or gold-leaf electroscope.

Radium salts are bought and sold in the United States almost entirely on the certificate of the Bureau of Standards. The measurements are made electroscopically by the γ-ray method, using standards that have been compared with the International standard in Paris. Every radium laboratory should have at least one secondary standard that has been certified by the Bureau of Standards.

Radium emanation, which is now quite largely used therapeutically instead of radium itself, may be measured by the γ-ray method exactly as radium, and is expressed in equivalent units, one curie being the amount of emanation in equilibrium with one gram of radium element. It is necessary only to allow the emanation to remain in a closed vessel for 4 hrs. to arrive at maximum γ-radiation before making the measurement. In making this measurement, one additional correction is necessary. On account of the short life of radium emanation (3.85 days half period) RaC lags behind in decaying by 0.8 per cent; and since it is RaC, not emanation, which furnishes the principal γ-rays, this correction must be deducted from the γ-ray indication to give the true quantity of emanation. If one wishes to know simply the γ-radiation and not the actual quantity of radium emanation, this correction is not necessary.

The writer is indebted to the Denver Fire Clay Company for Figs. 2 and 3, and to the Sachs-Lawlor Company of Denver for permission to describe Mr. Elzi's arrangement shown in Fig. 1. The electroscopes described are made by the Sachs-Lawlor Company and distributed by the Denver Fire Clay Company.

THE DISTRIBUTION OF CERTAIN CHEMICAL CONSTANTS OF WOOD OVER ITS PROXIMATE CONSTITUENTS

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INTRODUCTORY

In a previous paper,[1] the author has proposed a scheme for separating wood into a number of proximate groups. In addition to the groups designated, certain organic radicals (such as $CH_3.O$ and $CH_3.CO$) are known to occur in woods. Any given species is characterized by definite contents of these radicals which have accordingly become quite generally recognized as constants for that particular wood. They found no place in the proposed scheme for the reason that the quantitative relations between these so-called constants and the proximate groups were not known and it appeared likely that their inclusion would produce an overlapping of constituents. The purpose of the present investigation has been to learn the relations existing between the more important constants and proximate groups. Experiments have, therefore, been conducted to ascertain the distribution of (1) furfural-yielding groups, (2) acetic-yielding groups, and (3) methoxy groups, over the two chief proximate groups—cellulose and lignin.

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[1] *Loc. cit.*

[1] THIS JOURNAL, **11** (1919), 556.

The three above-mentioned constants have been considerably investigated. The pioneer work of DeChalmot[1] on the furfural-yielding complex and of Benedikt and Bamberger[2] on the methoxy groups has resulted in quantitative data for the most important woods and fibrous products and considerable information as to the relation of these data to the life history of the plant. Cross and Bevan[3] have studied the production of acetic acid from the lignocelluloses by various reactions of decomposition. Of these reactions, acid hydrolysis may probably be safely taken as a measure of the acetic-yielding groups preëxistent in the woods, which according to these authors are not acetyl groups, CH_3CO, but acetic residue groups $CH_2.CO$.[4] Schorger[5] has recently reported values for all three of these constants for a number of American woods.

The yields of acetic acid by hydrolysis and methoxy groups by the Zeisel method have a considerable industrial significance as measures, respectively, of the maximum commercial yields of acetic acid and wood alcohol obtainable by destructive distillation. The fact that the full yield of these substances is never realized industrially, due to losses by secondary reactions,[6] detracts from the practical value of their determination. On the other hand, it affords an incentive for the improvement of the manufacturing processes in the direction of a closer approach to theoretical yields. The furfural yield is not a measure of valuable products in the wood, but its determination in finished products has been used to give information as to the source of raw materials used in their manufacture.[7]

While precise information is lacking as to the relation of these constants to cellulose and lignin, certain opinions have found considerable support. The methoxy group is generally recognized as being closely connected with the lignin complex and the methoxy determination has been proposed as a measure of the lignin content.[8] The furfural-yielding groups have been found to be partly associated with the cellulose and partly with the lignin. W. E. Cross[9] has concluded from his experiments that the groups yielding acetic acid by hydrolysis are contained in the lignin and absent from the cellulose portion of woods.

The extent to which any of these radicals remain attached to either the cellulose or lignin, when lignocellulose is subjected to reactions of decomposition, must necessarily depend very much upon the nature and intensity of these reactions. The experiments herein described were conducted to ascertain the distribution of the constants under certain specified conditions, namely, those of the analytical determinations of cellulose and lignin. The results may therefore be taken to indicate whether the constants are to be regarded as groupings attached to and subordinate to these chief proximate groups, or as possessing an independent existence and themselves entitled to rank as proximate groups.

EXPERIMENTAL

The experiments were confined to redwood (*Sequoia sempervirens*). A quantity of sawdust was obtained by making a number of cross-sectional cuts through a redwood slab. The mixture of coarse and fine sawdust was sifted through a 50-mesh screen and the selected fine material used for the various determinations. The samples were analyzed in the air-dry condition with a moisture content of 11.62 per cent.

PREPARATION OF EXTRACTED WOOD—Portions of 2 g. were weighed into alundum thimbles and extracted in a Soxhlet apparatus for 6 hrs. with benzene, then for a further 6 hrs. with 95 per cent alcohol. The substance was then transferred to Gooch crucibles, containing as a filtering medium disks of mercerized cotton cloth, and washed with distilled water. Material so prepared is regarded as purified lignocellulose free from extractives.

PREPARATION OF CELLULOSE—Two grams of the wood, extracted as above, were subjected to the alternate action of chlorine and hot 3 per cent sodium sulfite solution in accordance with the procedure of Sieber and Walter.[1] The moistened material was placed in a Gooch crucible and the gas drawn through it by suction for 4 periods of 20, 15, 15, and 10 min. After each chlorination the residue was treated with half saturated sulfurous acid, washed with hot water, digested in 3 per cent sodium sulfite solution for 45 min., filtered off, and washed thoroughly with hot water. After the final treatment the residue was dried for 16 hrs. at 100° C.

PREPARATION OF LIGNIN—Two grams of the wood were extracted as before, partly dried at 60° C. and placed in a 750 cc. Erlenmeyer flask. 20 cc. of 72 per cent sulfuric acid were added and the flask rotated so as to bring all parts of the sawdust in contact with the acid. It was then allowed to stand 3.5 hrs. Fifty cc. of cold water were added, followed by 500 cc. of hot water, the mixture filtered on a Gooch crucible containing a cloth filtering disk, washed and dried for 16 hrs. at 100° C.

ANALYTICAL METHODS FOR DETERMINING THE CONSTANTS

FURFURAL-YIELDING GROUPS—These were determined by distillation of the material with 12 per cent hydrochloric acid (sp. gr. 1.06) and precipitation of the furfural in the distillate with phloroglucine, according to the method described by Schorger for pentosans.[2] No correction was made for methyl furfural, the total precipitate being calculated to furfural.

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[1] *Am. Chem. J.*, **16** (1894), 218; Cross and Bevan, "Cellulose," p. 181.

[2] *Manatsh.*, **11** (1890), 260; "Cellulose," p. 188.

[3] "Cellulose," p. 191.

[4] Cross and Bevan, "Researches on Cellulose," **3**, 103.

[5] THIS JOURNAL, **9** (1917), 560.

[6] Palmer, *Ibid.*, **7** (1915), 633; Schorger, *Ibid.*, **9** (1917), 556.

[7] Tollens, *J. Soc. Chem. Ind.*, **26** (1907), 987.

[8] Benedikt and Bamberger, *Loc. cit.*

[9] *Ber.*, **43**, 1526.

[1] *Papier-Fabr.*, **11**, 1179; *Chem. Abs.*, **8** (1914), 1202.

[2] THIS JOURNAL, **9** (1917), 558.

ACETIC-YIELDING GROUPS—The material was hydrolyzed by heating for 3 hrs. under a water-cooled reflux condenser with 100 cc. of 2.5 per cent sulfuric acid. The mixture was quickly filtered into a 750 cc. flask to avoid the introduction of carbon dioxide and washed with CO_2-free water to a total volume of about 200 cc. The acetic acid in the solution was then distilled off and determined by means of the following apparatus:

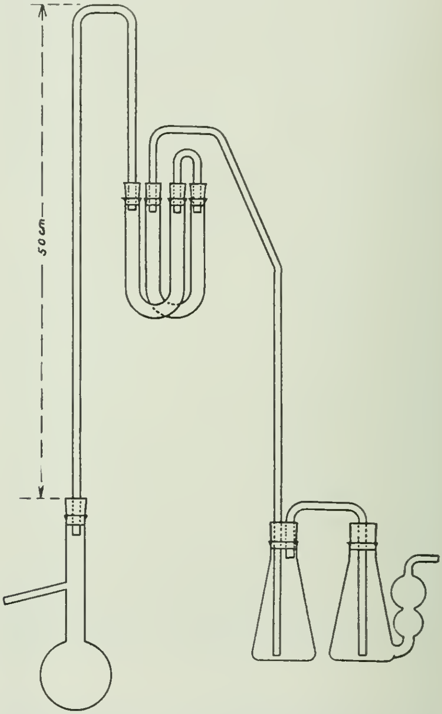
The 750 cc. flask was placed in a paraffin bath and closed by a rubber stopper containing a glass stopcocked funnel tube and a delivery tube. The funnel tube served to introduce CO_2-free water during the distillation and was protected by a soda lime tube attached to its open end by means of a rubber stopper. The delivery tube bent downward and terminated in a vertical condenser. This in turn was connected by a rubber stopper to a suction filter flask which served as a receiver for the distillate.

Suction was applied to the receiver and the paraffin bath raised to and maintained at 85° C. Higher temperatures were avoided as tending to the formation of formic acid from the hexose carbohydrates present. When most of the liquid had distilled over from the flask, 100 cc. of CO_2-free water were introduced and distilled over, after which the procedure was repeated with a second 100 cc. The total distillate was then removed and titrated with standard sodium hydroxide solution using phenolphthalein as indicator. The results, representing "total volatile acids," were expressed as acetic acid.

To obtain the actual acetic acid it was necessary to correct for the formic acid invariably present. A few cc. of silver nitrate solution were added to the solution after titration and the mixture left upon the steam bath for several hours. The silver formate was thereby decomposed, yielding an amount of metallic silver corresponding to the formic acid present. The precipitated silver was filtered off, washed, dissolved in dilute nitric acid, precipitated as silver chloride, filtered off, washed, ignited, and weighed. From the weight of silver chloride so obtained the amount of acetic acid equivalent to the formic acid was calculated by multiplying by the conversion factor 0.4. This result, deducted from the total acidity as found above, gave the actual acetic acid present.

METHOXY GROUPS—Methoxy groups were determined by the Zeisel method.[1] The apparatus and procedure here described have been found to give consistent results.

The decomposition flask was a small distillation flask (of about 130 cc. capacity) having its side tube connected with a carbon dioxide generator. In the mouth of the flask was placed a perforated cork carrying a delivery tube. This delivery tube ran vertically for 50 cm. and so acted to some extent as a reflux condenser and fractionating column. It then made two right-angled bends and, descending, was connected at its lower extremity with two U-tubes in series. The first of these contained distilled water and a few milligrams of phosphorus, the second distilled water only. The U-tubes were placed in a beaker of water arranged to be heated by a Bunsen burner. From the second U-tube, a delivery tube ran to the absorption apparatus which consisted of an Erlenmeyer flask and a Fresenius nitrogen bulb. The general arrangement and dimensions of the apparatus are shown in the accompanying figure. The paraffin and water baths and the carbon dioxide generator are omitted.



In the first and second absorption flasks were placed 35 and 15 cc., respectively, of freshly filtered alcoholic silver nitrate solution. (The solution was prepared by dissolving 10 g. of solid silver nitrate in 25 cc. of water and adding 225 cc. of 95 per cent alcohol.) 0.3 g. of material was placed in the decomposition flask and 15 cc. of hydriodic acid (1.70 sp. gr.) were added. The mixture was heated to 130° C. on a paraffin bath and the temperature maintained at 130° to 140° C., while a slow stream of carbon dioxide was passed through the apparatus. The beaker of water surrounding the U-tubes was kept at a temperature of 50° to 60° C. throughout the process. The operation was continued until the precipitated silver iodide in the absorption apparatus settled out, leaving a clear supernatant liquid, indicating the completion of the reaction.

The apparatus was then disconnected and the contents of the absorption flasks rinsed into a 600 cc. beaker. Water sufficient to make about 500 cc. was added and the whole evaporated on the steam bath to a volume of 150 to 200 cc. in order to expel the alcohol. A few drops of nitric acid were added, the solution again diluted to about 500 cc. and allowed to stand on the steam bath for about one-half hour for the silver iodide to settle. The precipitate was then collected in a tared asbestos Gooch crucible, washed, dried at 130° C. for 2 hrs., and weighed. CH_3O was calculated from the weight of silver iodide by multiplying by the factor 0.132.

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[1] *Monatsh.*, 6 (1885), 989; Meyer-Tingle, "Determination of Radicals in Carbon Compounds," John Wiley & Sons, Inc., p. 38.

By the above methods the furfural yield, acetic yield on hydrolysis, and methoxy yield were determined upon the raw wood, extracted wood, cellulose, and lignin. The results are shown in the table.

DISTRIBUTION OF GROUPINGS IN REDWOOD

Expressed in Percentages of Air-Dried Wood (11.62 Per cent Moisture)

	Furfural Yield	Total Volatile Acids by Hydrolysis	Formic Acid Expressed as Acetic	Actual Acetic Acid by Difference	Methoxy Group
Raw Wood	5.73	0.94	0.16	0.78	5.46
	5.95	1.03	0.16	0.87	5.74
AVERAGE	5.84			0.83	5.60
Extracted Wood	5.77	0.75	0.09	0.66	5.33
	5.65	1.03	0.06	0.97	5.35
AVERAGE	5.71			0.82	5.34
Cellulose	2.36	0.75	0.21	0.54	0.35
	2.69	0.66	0.10	0.56	....
AVERAGE	2.52			0.55	0.35
Lignin	0.24	0.09	....	0.09	5.49
	0.23	0.09	....	0.09	5.78
AVERAGE	0.24			0.09	5.63

Determinations were also made of the furfural yield of the filtrates and washings from the cellulose determination. The combined solutions from four determinations or 8 g. of wood were evaporated to somewhat less than 500 cc., placed in a 500 cc. volumetric flask, and diluted to the mark. 125 cc. aliquots corresponding to 2 g. of original wood were placed in the distilling flasks and mixed with 30 cc. of concentrated hydrochloric acid. The determination was then carried out as usual. Three determinations gave 2.30, 2.08, and 2.08 per cent of furfural in the chlorination liquors, the results being referred to the weight of air-dried wood.

Determinations of the methoxy group were made upon portions of lignin that had been hydrolyzed by boiling with 2.5 per cent sulfuric acid for 3 hrs. after being separated by the usual treatment with 72 per cent sulfuric acid. The methoxy content based on the original wood was 4.08 and 3.88 per cent. There is accordingly an average loss of 1.65 per cent of methoxy during the hydrolysis. Separate experiments have shown that the weight of lignin after the treatment is about 2 per cent less than when prepared in the usual manner. From the above results it is evident that the loss in weight of lignin is due chiefly to the splitting off of the methoxy group.

DISCUSSION

The foregoing results indicate that none of the three radicals investigated is to be regarded as existing entirely independent of the proximate constituents cellulose and lignin. Apparently they are so related to these substances that, when lignocellulose is attacked by hydrolytic reactions, they tend to remain at least partially joined to the cellulose or the lignin or to both.

No method is known whereby lignocellulose may be separated so as to yield both cellulose and lignin unchanged, but in every case one of them is obtained as a residue while the other is converted into alteration products and removed. It is therefore unsafe to draw the conclusion that radicals found with either cellulose or lignin, or both, exist similarly associated with them in the original lignocellulose complex. The radical is rather to be regarded as occupying an intermediate position between these chief proximate constituents, and remaining with the residue according to the extent that it resists the treatment employed. The same portion that remains with the cellulose under the conditions of one type of decomposition may remain with the lignin under another set of conditions.

A comparison of the data for raw and extracted wood shows that none of the three constants examined is materially affected by treatment with non-hydrolyzing solvents.

About half of the furfural-yielding complex remains in the cellulose residue. Most of the remaining portion is found in the chlorination liquors. As was pointed out in a previous paper[1] this last portion is probably due to xylan or other true pentosan existing as such in the wood, while the non-hydrolyzable furfural-yielding material contained in the cellulose is probably oxycellulose. The amount of furfural-yielding material remaining with the lignin is almost negligible.

The amount of acetic acid present in redwood is small and its determination is rendered uncertain by the presence of formic acid either preëxisting or produced by the action of the hydrolyzing acid upon hexoses. No general conclusions can therefore be drawn in regard to its distribution but it appears to be associated chiefly with the cellulose constituent. With the lignin there is very little. The combined amount found with the lignin and cellulose is slightly less than the total amount in the wood, indicating that part of the acetic-yielding groups separates independently. In view of the small quantities involved the results are not conclusive. In the case of redwood, and probably also in the case of other coniferous woods, which yield only small amounts of acetic acid on hydrolysis, it would appear that acetic acid should not be considered as an independent proximate group but as a radical already largely accounted for in the cellulose and lignin residues. This conclusion probably does not apply to hardwoods, where the acetic yield is much higher.

The methoxy groups are found quantitatively in the lignin constituent, directly confirming the frequent assertion that methoxy is a purely lignin characteristic. This occurs only when lignin is separated by the method described and subsequent hydrolysis avoided. If this is not done there is considerable splitting off of the methoxy groups.

These facts have an important bearing upon the proximate analysis of wood. A summative analysis of a wood may be made by drying, extracting with benzene and alcohol, and determining the cellulose and lignin in the manner previously described. It appears from the foregoing results that, when this is done, the cellulose and lignin constituents account for all of the methoxy group, nearly all of the acetic-yielding groups, and about half of the furfural-yielding groups. Except for the furfural due to hydrolyzable pentosans found in the chlorination washings, these constants are not to be regarded as proximate constituents but rather as radicals connected with the constituents cellulose and lignin. With the exception noted, these constants may be ignored in the summative analysis of coniferous woods.

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[1] Dore, THIS JOURNAL, **12** (1920), 264.

SUMMARY

I—A study is made of the distribution of the groups contained in redwood which yield furfural, acetic acid, and methoxy, with the object of learning their relation to the constituents cellulose and lignin.

II—About half of the furfural-yielding groups are associated with the cellulose, but only a small amount with the lignin. The portion present as true pentosan is hydrolyzed and removed during chlorination.

III—The acetic-yielding groups are partly associated with the cellulose, much less so with the lignin. A small amount appears to be detached from either. The results are not conclusive in view of the small amount present in redwood and the analytical difficulties. In the case of coniferous woods acetic acid probably need not be considered as a proximate group.

IV—The methoxy groups are wholly associated with the lignin. They may be partially split off from it by acid hydrolysis.

V—In the summative analysis of coniferous woods, all of the acetic-yielding and methoxy groups and part of the furfural-yielding groups may be disregarded as already accounted for in the cellulose and lignin. The furfural-yielding substances contained in the chlorination washings and representing hydrolyzed pentosans should be estimated.

THE PROXIMATE ANALYSIS OF CONIFEROUS WOODS

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Received November 18, 1919

INTRODUCTORY

A method has been recently proposed by the author for the summative proximate analysis of woods.[1,*] Later investigations have shown the advisability of certain modifications of the original scheme which are considered in detail in this paper.

The proposed system for the analysis of wood effected a separation of the wood substance into the following fractions: loss on drying, benzene extract, alcohol extract, water-soluble, soluble in one per cent sodium hydroxide, cellulose, and lignin. Full information as to the composition of these fractions was lacking, but it was believed that the wood constituents were separated into logical groups based upon chemical similarity and economic value.

The scheme was found to account for nearly all of the material of coniferous woods in that the sum of all constituents varied from 96 to 97 per cent for the three conifers examined. With the hardwoods the method was unsuccessful, as 10 to 17 per cent of the constituents remained unaccounted for. The available data seem to indicate that the chemistry of the hardwoods is an entirely separate problem. The woods of the broad-leaved trees have accordingly been omitted from consideration in this investigation and the conclusions are applicable to the conifers only.

DEFECTS IN PROPOSED SCHEME

(1) ITS FAILURE TO GIVE CORRECT RESULTS FOR CELLULOSE AND LIGNIN—It was noted in the original paper[1] that when digestion in one per cent sodium hydroxide was used less cellulose and lignin were obtained than when this treatment was omitted. In a subsequent paper[2] it was shown that the diminished yield of cellulose was due to partial destruction of true cellulose instead of to greater purity of the product. Accordingly the results for cellulose are incorrect. No direct data are available for lignin, but it has been shown in the preceding paper that lignin readily loses a portion of its methoxy groups when it undergoes acid hydrolysis. Possibly the same effect is produced by alkalies.

(2) THE VAGUE SIGNIFICANCE OF THE WATER-SOLUBLE AND ALKALI-SOLUBLE FRACTIONS—In the absence of detailed studies of the substances contained in these portions, it was believed that they consisted of substances corresponding approximately to König's "proto" and "hemi" forms of cellulose and lignin.[3] It is apparent from subsequent studies,[2] however, that they contain also degradation or hydrolytic products of true cellulose and true lignin. The numerical expression of these fractions has therefore no value as an analytical statement of wood constituents.

(3) THE FAILURE TO EXPRESS THE HEMICELLULOSES—Schorger's studies of mannan[4] and galactan[5] have shown that these carbohydrates are found in all conifers, sometimes in considerable quantity. Xylan is well known as a constituent of woods. It is therefore evident that a complete analysis of a wood should take these hemicelluloses into consideration. In the proposed scheme the water- and alkali-soluble portions only partially accounted for these bodies together with other substances.

(4) ORGANIC RADICALS—The original scheme took no account of organic radicals present—the so-called "wood constants." The preceding paper has shown that, with the exception of the furfural-yielding substances soluble in the chlorination washings, these radicals may be disregarded as proximate constituents of coniferous woods.[6] The original scheme is defective, however, in that it ignores this soluble furfural-yielding substance.

The remedies for the above defects are quite evident. The cellulose and lignin determinations should be made reliable by omission of the alkaline hydrolysis. The water- and alkali-soluble fractions would disappear, leaving the hemicelluloses entirely unaccounted for. It would then be necessary to give the hemicelluloses a separate place in the scheme, and methods would be required for their estimation either collectively or individually. The soluble furfural-yielding substance (probably the pentosan, xylan) would be included in the hemicelluloses.

The present investigation is an attempt to revise the original scheme in accordance with the above suggestions. Methods have been applied for the determination of the hemicelluloses. The revised procedure has then been checked by making these and the other determinations required for a complete summative analysis on the three coniferous woods formerly employed.

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* Numbers refer to Reference, page 479.

EXPERIMENTAL

The woods examined were redwood (*Sequoia sempervirens*), yellow pine (*Pinus ponderosa*), and sugar pine (*Pinus lambertiana*). The original material was in the form of slabs. In the case of the redwood it represented mostly sapwood with a small amount of the outer portion of heartwood. In the case of the pines it represented sapwood only.

The samples were in the form of fine sawdust obtained by making a number of cross-sectional cuts of the slabs and screening the resultant material through a sieve having 50 meshes to the linear inch. As considerable coarse material was rejected, the samples cannot be regarded as strictly representative of the original material. That, however, is of no importance to the purpose of this study which was to determine the applicability of the analytical methods to the woods employed.

ANALYTICAL METHODS

LOSS ON DRYING—Two grams of the wood were dried at 100° C. to constant weight.

BENZENE EXTRACT—Two grams of material dried as above were placed in an alundum thimble and extracted in a Soxhlet apparatus for 6 hrs. with benzene. The solvent was then evaporated and the residual extract dried for 1 hr. at 100° C., and weighed.

ALCOHOL EXTRACT—The residue from the above treatment was extracted for 6 hrs. with 95 per cent alcohol. The solvent was evaporated and the residue dried and weighed as before.

CELLULOSE—Two grams of material after extraction with benzene and alcohol as above were transferred to a Gooch crucible containing a cloth filtering disk and washed with distilled water. The cellulose was determined by the Sieber and Walter method as described in the preceding paper and elsewhere.[7] The residues were tested for lignin by digestion in 72 per cent sulfuric acid and when appreciable amounts were found, the lignin was filtered off and weighed, and the cellulose corrected for it.

LIGNIN—Two grams of material after extraction with benzene and alcohol were air-dried at low temperature (60° C.) and transferred to a 750 cc. flask. 20 cc. of 72 per cent sulfuric acid were added and the mixture allowed to stand at room temperature for 3.5 hrs. 50 cc. of cold water were added, then 500 cc. of hot water. The residue was filtered off on a tared Gooch crucible, washed thoroughly with hot water, dried, and weighed.

HEMICELLULOSES—The hemicelluloses are apparently contained quantitatively in the chlorination washings,[2] and it was thought at first that these solutions might be utilized for their determination. They were found to be unsatisfactory for this purpose except in the case of the soluble pentosans. The presence of lignin derivatives interferes seriously with either the collective estimation of the hemicelluloses by reducing sugar methods or the separate mannan and galactan determinations.

SOLUBLE PENTOSANS—The chlorination filtrates and washings from four cellulose determinations representing 8 g. of original material were evaporated to a little less than 500 cc., transferred to a 500 cc. volumetric flask and made up to volume. Aliquot parts of 125 cc. each were placed in the distilling flask of the pentosan apparatus, 30 cc. of concentrated hydrochloric acid added, and the furfural distilled off in the usual manner. The furfural was precipitated as phloroglucide, and the precipitate filtered off, washed, dried, and weighed. The results were calculated to xylan by means of Krober's tables.

MANNAN—The method used was that described by Schorger.[8] Ten grams of the wood were hydrolyzed by boiling for 3.5 hrs. with 150 cc. of hydrochloric acid (sp. gr. 1.025) in an Erlenmeyer flask under a reflux condenser. The mixture was then filtered and the residue rinsed into a beaker and digested with 100 cc. of water for a few minutes on the hot plate. The solution was poured through the filter and the residue again rinsed back into the beaker and the digestion repeated. This process was continued until about 500 cc. of filtrate were obtained. The filtrate was neutralized with sodium hydroxide and the solution made slightly acid with acetic acid, after which it was evaporated to 150 cc. It was filtered into a glass-stoppered Erlenmeyer flask, and a mixture of 10 cc. of phenylhydrazine and 20 cc. of water acidified with glacial acetic acid was added. The mannose hydrazone was in every case immediately precipitated. The whole was allowed to stand for 2 hrs. with frequent shaking and then filtered on a Gooch crucible fitted with a filtering disk of mercerized cotton cloth. It was washed several times with cold water and then with acetone, dried at 100° C. and weighed. The weight of residue was calculated to mannan by multiplying by the factor 0.6.

GALACTAN—Five grams of the material were placed in a 100 cc. beaker, and 60 cc. of nitric acid (sp. gr. 1.15) were added. The beaker was placed in a water bath and the liquid evaporated to about 20 cc., care being taken not to allow the temperature of the water bath to exceed 87° C. The mixture was then diluted to about 75 cc. with hot water, and filtered. The residual cellulose was washed until the filtrate came through practically colorless. A total volume of about 250 cc. was generally thus obtained. The filtrate and washings were evaporated on the water bath at 87° C. to a volume of about 10 cc. The residue was set aside for several days to allow the mucic acid to separate out. Large crystals (possibly oxalic acid) always formed at first, then a day or two later fine flakes of mucic acid separated out. At this point the mixture was stirred vigorously to facilitate the precipitation. About 24 hrs. after the mucic acid appeared the mixture was diluted with 20 cc. of cold water. The larger crystals redissolved leaving the mucic acid unaffected. After a further 24 hrs. standing, the mucic acid was filtered off on a tared asbestos Gooch crucible and washed with about 50 cc. of water, 60 cc. of alcohol, and several times with ether. It was then dried at 100° C. for 3 hrs. and weighed. Galactan was calculated by multiplying the weight of residue by the factor 1.2.

RESULTS

By the foregoing methods the following results were obtained for the three coniferous woods examined. The figures are in every case averages of two or more determinations. In the first three columns are given the results on air-dry material as found by analysis; in the second three, the same results are recalculated to the oven-dry basis.

ANALYSES OF WOODS (Results in Percentages)

	AIR-DRY BASIS			OVEN-DRY BASIS		
SAMPLE NO.	1	2	3	1	2	3
	Redwood	Yellow Pine	Sugar Pine	Redwood	Yellow Pine	Sugar Pine
Loss on drying at 100° C.	11.62	8.98	9.84	....	....	....
Benzene extract	0.30	2.02	2.56	0.34	2.22	2.84
Alcohol extract	3.88	1.36	1.71	4.39	1.49	1.90
Cellulose	48.51	52.54	53.36	54.89	57.72	59.18
Lignin	30.49	26.82	26.60	34.50	29.47	29.50
Soluble pentosans (as xylan)	3.24	3.18	1.68	3.67	3.49	1.86
Mannan	2.84	5.80	5.98	3.21	6.37	6.63
Galactan	0.44	0.71	0.45	0.50	0.78	0.50
TOTAL	101.32	101.41	102.18	101.50	101.54	102.41

DISCUSSION OF METHODS

CELLULOSE—It has been previously shown that the method here practiced (omission of preliminary hydrolysis) gives the maximum yield of cellulose free from hemicelluloses and lignin. The process therefore conforms to the requirements of an accurate cellulose method and the product to the proposed definition of a true cellulose derived from lignified material.[2]

LIGNIN—The term "lignin" has not yet been defined with sufficient precision to permit a comparison of the product with exact specifications. Lignin is generally understood to denote the non-cellulose portion of the wood tissue proper and this conception implies its freedom from extractives, hemicelluloses, and cellulose. The most accurate method for lignin is therefore the one that yields the greatest amount of the substance with the highest purity according to the above standards.

It is believed that there is sufficient evidence to justify the claim that the method used conforms to these requirements. Both acid and alkaline hydrolysis result in diminished yield of product and it has been shown that this is due (at least in the former case) to a partial splitting off of the methoxy groups which are characteristic portions of the lignin complex. Accordingly, only by the complete omission of hydrolysis is the full yield of lignin obtainable.

Inasmuch as the lignin disappears completely on being submitted to the alternate action of chlorine gas and sodium sulfite solution, it is free from cellulose which would otherwise remain as a residue. On hydrolyzing with 2.5 per cent sulfuric acid no reducing sugars were obtained, so the material is free from hemicelluloses. The preliminary treatment with benzene and alcohol precludes the possibility of the presence of extractives. The residue may be therefore considered "pure" in accordance with the requirements outlined.

SOLUBLE PENTOSANS—Dilute alkaline solutions have been recommended for extracting xylan or wood gum from the hard woods.[9] It has been asserted, however, that the wood gum of coniferous woods is much less readily soluble in alkaline solvents than that from the wood of the broad-leaved trees.[10] For this reason it appeared to be desirable to use the chlorination liquors for the determination of soluble pentosans.

MANNAN—The method gave results that were in good agreement with each other and consistent with those given by Schorger[11] for the corresponding woods. Small portions of the residue, recrystallized by alcohol, gave a melting point of 188° C.

GALACTAN—In their paper on the galactan of the western larch, Schorger and Smith[12] report only traces of soluble galactans in the coniferous woods examined. In their experiments 100 g. of the material were digested several times in hot water and the resulting solution evaporated nearly to dryness and treated with nitric acid in the usual manner. Other investigators,[13] however, have reported the presence of galactan in sulfite waste liquors, indicating that galactans are contained in some of the paper-making woods. It therefore seemed probable that galactans are present in not readily soluble form. Accordingly no attempt was made in the present investigation to extract the galactan as such from the wood by means of solvents. Instead the procedure of attacking the wood directly with nitric acid was decided upon as the best means of giving the full galactan content of the wood.

The evaporation of the wood substance with nitric acid results in the production of a large amount of insoluble oxycellulose which interferes with the separation of the mucic acid. This difficulty was overcome by the procedure devised by Miyake[14] in which the mixture, after evaporation, is diluted, and the solution containing the mucic acid is filtered off from the insoluble matter and again evaporated.

The author has pointed out the uncertainty of yield of mucic acid by the usual process when only small amounts of galactan are present.[15] Schorger and Smith[16] have shown that much better results are obtained if the temperature is not allowed at any time to exceed 87° C., instead of maintaining the bath at 94° to 96° C., as prescribed in the official method for galactan.[17] The use of the lower temperature has accordingly been adopted.

Considerable difficulty was encountered at first in obtaining a crystallization of the mucic acid after evaporation. This appeared to be due chiefly to the interfering action of oxalic acid or other substances contained in the solution. When the latter was evaporated to the usual volume of 20 cc., no separation of mucic acid occurred even after several days' standing. By evaporating to a smaller bulk clear crystals separated out after one or two days. These crystals on standing increased in size and a day or two later the characteristic mucic acid flakes were precipitated. After the last precipitation was judged to be complete, the larger crystals were easily removed by diluting the solution to the usual volume of 30 cc. The amounts of residue were always too small to permit of a melting-point determination but the appearance of the precipitate was such as to leave little doubt that it was actually mucic acid.

Considering the nature and difficulties of the method, the agreement of results may be considered satisfactory. Redwood gave 0.40 and 0.47 per cent; yellow pine gave 0.96, 0.66, 0.43, and 0.80 per cent; sugar pine gave 0.55 and 0.35 per cent of galactan. It is believed that the described procedure gave approximately correct results. A critical study of the whole galactan method is still much needed, however.

DISCUSSION OF RESULTS

It is believed that analyses of coniferous woods made by the methods described account for all important constituents of those woods. The sum is in every case slightly over 100 per cent but not more so than might be expected from the character of the methods employed. A variation of several tenths of a per cent between duplicate determinations is usual. The cellulose and lignin are probably always slightly overestimated on account of the practical impossibility of getting complete contact between all particles of the material and the attacking reagents. This difficulty could be partly overcome by better mechanical condition of the wood.

The possibility of overlapping of values due to certain constituents being included in more than one determination has received careful consideration throughout these investigations. It is believed that such double estimations have been largely avoided. Most of the proximate groups can be shown to be free from any of the constituents contained in the other groups. It has already been pointed out that this is true in the case of cellulose and lignin. Mannan and galactan determinations depend upon reactions too specific to admit of the inclusion of other constituents.

By improving the mechanical condition of the sample in respect to fineness, better results should be obtained in all the determinations. Some of the determinations, particularly that of galactan, could probably be made more accurate and reliable. These changes would no doubt give a considerably better summation and a consequently more satisfactory accounting of the constituents of the coniferous woods.

SUMMARY

1—An improved procedure is described for the summative analysis of coniferous woods. Methods are given for the estimation of the following constituents: loss on drying, benzene extract, alcohol extract, cellulose, lignin, soluble pentosans, mannan, and galactan.

2—By the omission of preliminary hydrolysis, more reliable results are obtained in the cellulose and lignin determinations than by methods previously used.

3—Soluble pentosans are determined in the chlorination liquors, mannan and galactan on separate portions of the original material. Improvements in the galactan determination are described.

4—Complete analyses of redwood, yellow pine, and sugar pine are carried out by these methods. A summation of slightly over 100 per cent is obtained in every case.

5—The results indicate that overlapping of the proximate groups, *i. e.*, partial inclusion of any constituent in more than one group, has been largely avoided.

6—Analyses by the proposed scheme probably account for all important constituents of coniferous woods.

REFERENCES

1—This Journal, **11** (1919), 556.
2—*Ibid.*, **12** (1920), 264.
3—*Z. Nahr. Genussm.*, **28** (1914), 177.
4—This Journal, **9** (1917), 748.
5—Schorger and Smith, *Ibid.*, **8** (1916), 494.
6—Dore, preceding paper, p. 472.
7—Sieber and Walter, *Chem. Abs.*, **8** (1914), 1202; Johnsen and Hovey, *Paper*, [23] **21** (1918), 36; *J. Soc. Chem. Ind.*, **37** (1918), 132*t*.
8—This Journal, **9** (1917), 748.
9—Cross and Bevan, "Cellulose," p. 187.
10—Klason, Cross and Bevan, "Researches on Cellulose," **3**, 105; Schorger, This Journal, **9** (1917), 562.
11—*Ibid.*, **9** (1917), 749.
12—*Ibid.*, **8** (1916), 499.
13—Lindsey and Tollens, *Ann.*, **267**, 341; Klason, *Loc. cit.*; Hagglund, *Biochem. Z.*, **70** (1915), 416.
14—*Chem. Abs.*, **6** (1912), 2958; **8** (1914), 2007.
15—This Journal, **7** (1915), 721.
16—*Ibid.*, **8** (1916), 498 (footnote).
17—U. S Department of Agriculture, *Bulletin* **107**, 55.

THE DETECTION OF ARSENIC IN SULFUR

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Received October 23, 1919

A certain sample of sulfur was reported to contain arsenic. It had been tested by a method first devised by Schaeppi[1] and later accepted by many authorities.[2] We found that the sulfur contained no trace of arsenic, but that when it was tested by Schaeppi's method, a decided qualitative test for arsenic was obtained. On further investigation it was found that this method contains a fundamental error which makes it useless as a test for small quantities of arsenic.

The method as described by Schaeppi consists essentially in first digesting the sulfur with dilute nitric acid for the purpose of removing calcium chloride, sulfate, and sulfide. The sulfur washed free from acid is now treated with dilute ammonia solution for 15 min. at 70° to 80° C. Schaeppi assumes that any arsenic present in the sulfur must exist as sulfide, mainly arsenious sulfide, and will be dissolved by the ammonia. The arsenic is then estimated indirectly through determination of the amount of sulfide by precipitation with silver nitrate in neutral solution.

"For very rough estimations, it is sufficient to treat 10 g. of finely ground sulfur with nitric acid, to extract with ammonia, and to add silver nitrate. From the intensity of the color or the quantity of the precipitate of silver sulfide, it may be judged whether the sulfur is approximately free from arsenic or is strongly contaminated."[3]

Schaeppi endeavored to test the accuracy of his method by dissolving known amounts of pure arsenious sulfide in ammonia solution, carefully neutralizing with nitric acid, and titrating with decinormal silver nitrate using chromate as indicator. His results showed fairly good agreement between the quantities of arsenic taken and those found. However, his results would have been conclusive only if the arsenious sulfide had been added to the sulfur and the mixture tested by his method. Any other sulfide if present in the ammonia solution would also be precipitated by the silver nitrate. As a matter of fact, we found that sulfur continuously reacts with dilute ammonia at 70° to 80° C. to form sulfides, so that even arsenic-free sulfur will give a qualitative test for arsenic by this method.

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[1] *Chem. Ind.*, **4** (1881), 409.

[2] Crooks, "Select Methods of Chemical Analysis," 4th ed., 416; Lunge, "Technical Methods of Chemical Analysis," **1** (1908), 267; Lunge, "The Technical Chemist's Handbook," 1916, 107.

[3] Crooks, *Loc. cit.*

EXPERIMENTAL

The sulfur used in these experiments was obtained from Texas deposits[1] and was found to be absolutely free from arsenic when tested by the Gutzeit method as described later in this paper.

Ten grams of a representative sample, powdered to pass a 160-mesh, were digested with 25 cc. of hot water, to which 0.4 cc. concentrated nitric acid was added. It was then washed free from acid and sulfides and digested with 25 cc. water and 0.5 cc. ammonium hydroxide (sp. gr. 0.90) at a temperature of 70° to 80° C. for 15 min.

The filtrate was somewhat tinged with a bright yellow color and gave a heavy dark brown precipitate on the addition of silver nitrate. The sulfur was now washed clean from alkali and sulfides and the extraction repeated with ammonia solution as before. Again the filtrate gave a heavy precipitate on the addition of silver nitrate.

The extraction was repeated a third and a fourth time, washing the sulfur clean from alkali and sulfur in each case and the same results were obtained. The precipitate with silver nitrate in the last extract seemed as heavy as that in the first.

A sample of flowers of sulfur was tested in the same way, the extraction with dilute ammonium hydroxide being repeated three times. The results were the same as in the case of the crude sulfur.

To determine whether the ammonium hydroxide solution really contained arsenic or not, the first extract from 10 g. of crude sulfur was acidified with hydrochloric acid, a crystal of potassium chlorate added, and the solution boiled until all the chlorate was decomposed. This solution was now tested by Gutzeit's method for arsenic and none was detected.

Further, 8 g. of crude sulfur were extracted with dilute ammonia at 70° to 80° C. The extract was acidified with strong nitric acid and evaporated to dryness on a water bath. A few cc. of concentrated nitric acid were added and was again evaporated to dryness. The residue was dissolved in water and tested by Gutzeit's method for arsenic with negative results. In a check test, 0.00004 g. of arsenic under similar conditions in the Gutzeit apparatus gave a well-marked arsenic stain.

These experiments indicate that sulfur reacts with dilute ammonium hydroxide at 70° to 80° C. to form ammonium sulfides. This is substantiated by the well-known fact that sulfur readily dissolves in hot solutions of the strong alkalies to form polysulfides. A sample of arsenic-free sulfur would, therefore, continue indefinitely to give a test for arsenic by Schaeppi's method.

TESTING THE SULFUR FOR ARSENIC BY GUTZEIT'S METHOD

To prepare the solution for the test, Scott[1] recommends the following procedure:

> Ten grams of the material (brimstone) are treated with 30 cc. of carbon tetrachloride mixture (3 parts CCl_4 + 2 parts Br) and after standing for 10 min. 25 cc. strong nitric acid are added in small portions (a watch glass covering the beaker during the intervals of addition). The mixture is taken to dryness on a steam bath, water is added, and the evaporation repeated. Arsenic is now determined on the residue by the Gutzeit method for arsenic.

In our experience 25 cc. of strong nitric acid were insufficient to oxidize the sulfur bromide even when added drop by drop from a pipette; 10 to 15 cc. more were needed, depending on the length of time the solution was allowed to stand on the water bath. It was found advisable to warm the sulfur bromide slightly before adding the nitric acid from a dropping pipette. The final evaporations were carried out directly over a flame, instead of on a water bath, until sulfur trioxide fumes appeared.

By the action of the bromine and nitric acid the sulfur is completely oxidized to sulfuric acid. The carbon tetrachloride is added to moderate the violence of the reaction and to prevent the precipitation of sulfur. Any excess of these reagents is expelled by the final evaporations. The acid solution remaining in the flask was now tested for arsenic by Gutzeit's method, details of which may be found in any standard textbook on chemical analyses.

The crude sulfur used in the work on Schaeppi's method was tested in this way with the following results:

1—Ten g. of sulfur gave no test for arsenic. At the completion of the test 1 cc. of 0.001 N As_2O_3 solution (0.00004 g. As) was added to the solution remaining in the Gutzeit apparatus and a strong test for arsenic was obtained in a few minutes. This proved that no substance was present which would prevent the arsenic test from showing, had arsenic been present.

2—Ten g. of crude sulfur to which 0.00004 g. As were added gave a distinct test for arsenic, quite comparable with the stain obtained when a solution containing an equal quantity of arsenic was tested directly in the Gutzeit apparatus.

SUMMARY

I—It has been found that sulfur reacts somewhat with dilute ammonium hydroxide at 70° to 80° C. to form sulfides.

II—Schaeppi's method of testing for arsenic in sulfur has been shown to contain a fundamental error due to this interaction of sulfur with dilute ammonium hydroxide.

III—The method of testing for arsenic in sulfur which consists in oxidizing the sulfur with bromine and nitric acid and testing the residue by Gutzeit's method for arsenic has been proved to be reliable.

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[1] From the recently developed deposits of the Texas Gulf Sulfur Co., at Gulf, Matagorda Co., Texas. The three great deposits of sulfur which are being worked commercially in the country (Union Sulfur Co., Freeport Sulphur Co., Texas Gulf Sulfur Co.) are all free from arsenic.

[1] *Loc. cit.*, 415.

BUTYL ALCOHOL AS A MEDIUM FOR THE DETERMINATION OF SAPONIFICATION NUMBERS[1]

By A. M. Pardee, R. L. Hasche and E. Emmet Reid

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Received October 7, 1919

In a recent article[2] it was shown that normal butyl alcohol is an excellent medium in which to conduct the quantitative saponification of esters. This suggested its use in the determination of the saponification numbers of fixed oils, fats, and waxes. The method of Koettstorfer[3] has, with little modification, been generally adopted.[4] That difficulties are met with is shown by the number of modifications that have been proposed. The chief trouble has been in getting some of the fats and waxes into perfect solution in the ethyl alcoholic potash.

Smithan[5] adds 20 cc. of ether, and Henriques[6] uses petroleum ether to aid solution in his cold saponification method.

Lewkowitsch[7] advises heating fats which are difficult to saponify under pressure, using copper bottles with screw caps.

Kossel and Obremueller treat the sample with absolute alcohol in which metallic sodium has been dissolved.

Wool fat has given much trouble. Lewkowitsch says "wool wax must be boiled with an excess of 0.5 *N* alcoholic potash for a least 24 hrs." Fabrion[8] has completely saponified it in an open capsule, on the water bath, with 2 *N* caustic soda, repeatedly boiling it almost to dryness to get rid of the water, and taking up the residue each time with strong alcohol.

Winkler[9] recommended the use of propyl alcohol, since it is a better solvent for fats and has a higher boiling point. He tried twelve oils, fats, and waxes, and obtained good results.

Normal butyl alcohol, boiling at a higher temperature than either ethyl or propyl alcohol, makes possible the use of higher temperatures for the saponification. Its longer hydrocarbon chain increases its solvent power for fats, waxes, etc. From the work of Anderson and Pierce[10] it appears that at 25° the saponification velocities of an acetate in methyl, ethyl, and isoamyl alcohols are in the ratio 1 : 7 : 15. From this saponification might be expected to proceed much more rapidly in normal butyl than in ethyl alcohol.

The simple method of Koettstorfer gives excellent results for the more common oils and fats and, by various modifications, special cases can be taken care of, but it is desirable to have a simple method which will be applicable to a wide variety of materials without extra precautions. The official directions read "boil for 30 min. or until the fat is completely saponified." The operator is thus required to observe and to decide when the "fat is completely saponified," since much longer time is required for some fats than for others.

The plan of the present study was to put a number of fats, oils, and waxes through identically the same treatment, making the manipulation as simple as possible in the hope of finding a simple routine method with wide application. For comparison, runs were made using ethyl alcoholic soda in the same volume as when butyl alcohol was used. It is the common practice to use considerably larger proportions of ethyl alcohol than this, so as to effect complete solution, and thereby excellent results are obtained. The comparison is simply between butyl and ethyl alcohol under these special conditions.

MATERIALS

The ethyl alcohol for making the standard solution was purified by treating with caustic potash and silver nitrate, and distilling. The normal butyl alcohol was used as obtained in the market. In each case, the alcoholic alkali was prepared by adding metallic sodium to the alcohol. The oils, fats, and waxes were the best commercial samples obtainable, rancid and discolored specimens being rejected. Those which appeared to contain water were dried at 110°. They were selected according to the groups given in Allen's "Commercial Organic Analysis."

EXPERIMENTAL PROCEDURE

One-gram samples were taken. The fats were weighed into 100-cc. round bottom Jena flasks, five of which, making a series, were fastened to a rack so that they could be lowered and raised simultaneously. They fitted into five openings in a steam bath and were provided with 3 ft. air condensers.

The oils were weighed into the saponification flasks from small Erlenmeyer flasks fitted with dropping pipettes. The waxes were cut into small cubes, while the butter, wool fat, and lanolin were weighed in small glass capsules.

To the material in the flask were added 10 cc. of the standard 0.5 *N* alcoholic alkali. The flask was placed immediately on the steam bath and heated exactly one hour when it was removed, 50 cc. carbon dioxide-free water added, and the excess alkali titrated with 0.5 *N* hydrochloric acid. In case the unsaponified material was high melting the mixture was kept hot during the titration.

As the butyl alcohol was nearly anhydrous, 0.5 cc. of water was added to each flask containing this alcohol, half an hour after the heating had begun, to provide for the saponification of the butyl ester, the formation of which is the first thing that takes place.

RESULTS

The results are given below in tables, the figures in each line representing simultaneous experiments. "E" designates the series in ethyl alcohol and "B" those in normal butyl alcohol. Under "Difference" is placed the percentage by which the average of the ethyl alcohol figures falls short of the butyl. Since it has been customary to give saponification numbers in terms of KOH, the results obtained with the sodium alcoholates have been calculated to this basis and are so put down in the tables.

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[1] Our thanks are due to Dr. G. S. Jamieson, in charge of Oil, Fat, and Wax Laboratory, U. S. Bureau of Chemistry, for several helpful criticisms. The experimental work was carried out at Washington and Jefferson College by A. M. Pardee and R. L. Hasche.

[2] This Journal, **12** (1920), 129.

[3] *Z. anal. Chem.*, **18** (1879), 199

[4] Official and Provisional Methods of Analysis, U. S. Dept. of Agr., *Bulletin* **107** (1911), 137; This Journal, **11** (1919), 1165.

[5] *Analyst*, **18** (1893), 193.

[6] *Z. angew. Chem.*, **1895**, 721.

[7] "Chemical Technology of Oils, Fats and Waxes," **1** (1909), 85.

[8] *Z. angew. Chem.*, **1898**, 268.

[9] *Ibid.*, **24** (1911), 636.

[10] *J. Phys. Chem.*, **22** (1918), 51.

Table I—Saponification Numbers in Ethyl and Butyl Alcohols

		Oils					Average	Percentage Difference
Castor	E	180.0	180.6	180.7	180.2	179.9	180.3	
	B	179.1	181.5	181.9	182.0	181.5	181.2	0.5
Coconut	E	247.1	248.7	249.1	...	248.3	...	
	B	250.0	249.6	249.8	250.8	...	250.0	0.7
Cod-liver	E	179.7	178.7	179.5	178.7	178.9	179.1	
	B	191.0	190.3	190.7	190.2	190.4	190.5	6.0
Cottonseed	E	190.3	189.6	190.2	190.2	...	190.1	
	B	193.2	187.6	193.5	189.3	193.5	191.4	0.7
Croton	E	204.8	206.1	206.4	206.1	205.1	205.7	
	B	225.7	225.4	224.7	225.1	225.1	225.3	8.7
Linseed	E	186.3	187.6	189.0	185.5	180.0	185.6	
	B	198.0	198.8	197.4	199.4	198.9	198.5	6.5
Neat's-foot	E	112.3	109.8	109.5	111.8	114.1	111.5	
	B	132.5	133.5	130.7	132.1	...	131.7	15.3
Palm	E	198.2	196.9	196.7	197.0	...	197.2	
	B	204.1	206.5	205.8	204.3	204.4	205.2	3.9
Peach Kernel	E	189.9	190.6	189.1	190.6	...	190.0	
	B	191.1	190.9	189.4	191.8	189.7	190.6	0.3
Rape Seed	E	169.0	167.3	168.0	168.7	168.3	168.3	
	B	175.9	176.5	174.1	175.2	174.5	175.2	4.0
Sesame	E	191.4	190.1	190.1	188.8	...	190.5	
	B	191.4	191.7	190.5	191.8	191.6	191.4	0.4
Sperm	E	133.4	132.1	134.2	134.0	134.1	133.5	
	B	147.7	148.6	147.7	147.3	148.7	148.0	9.7
Sperm, adulterated	E	136.7	138.1	137.7	138.7	139.0	138.5	
	B	151.4	152.7	153.4	151.1	151.3	152.0	8.9
		Waxes						
Beeswax, yellow	E	82.4	82.3	80.6	83.8	81.5	82.1	
	B	91.4	91.4	92.2	90.7	91.3	91.4	10.2
Beeswax, white	E	79.9	74.7	70.9	78.5	76.9	76.2	
	B	94.4	94.7	96.6	96.4	97.2	95.9	20.5
Spermaceti	E	114.9	116.2	114.3	...	...	115.2	
	B	126.0	125.2	126.3	125.3	126.2	125.8	8.5
		Fats						
Butter	E	227.9	219.3	223.3	219.4	221.0	220.5	
	B	232.4	230.6	229.4	231.5	228.6	230.5	4.3
Japan Wax	E	218.0	214.4	215.6	216.8	219.0	216.7	
	B	225.3	228.9	226.9	225.2	...	226.6	4.1
Tallow	E	185.8	182.6	181.8	184.5	183.6	183.7	
	B	197.1	198.7	199.0	198.3	...	198.3	7.4
Wool Fat, Anhydrous	E	101.3	98.2	98.1	...	...	99.2	
	B	(120.0)	11.16	112.5	114.2	113.2	112.9	12.1
Lanolin	E	56.4	51.0	48.3	49.1	48.1	50.6	33.4
	E[1]	70.0	70.5	70.6	70.7	...	70.4	
	B	76.5	74.6	77.3	76.4	75.2	76.0	7.3
	E	84.7	77.7	84.3	84.5	...	83.8	
	B	95.6	95.6	95.4	99.3	97.9	96.8	13.3
	E	67.8	66.8	67.7	66.9	...	65.5	
	B	79.5	80.0	82.4	78.6	79.4	80.0	18.0

[1] With absolute alcohol and sodium, according to Allen's "Commercial Analysis," **II**, 495.

It appears from these runs that substantially the same values are obtained in ethyl and butyl alcohols for the more readily saponified oils and fats, though the values in butyl alcohol are always somewhat higher. For substances that are more difficult to saponify, considerably higher and more reliable values are obtained in butyl alcohol than in the same volume of ethyl alcohol. Doubtless the ethyl alcohol values would have come up to the higher figures had larger amounts of alcohol been employed, or had the heating been continued till complete saponification had been effected. The figures obtained in butyl alcohol agree well with the accepted values. Our sample of neat's-foot oil must have been adulterated. The low results with tallow in ethyl alcohol are surprising. They were repeated with a different sample of tallow which gave higher figures but those for the two alcohols were in the same ratio.

In order to get some idea of relative rates of saponification in the two solvents, the following experiments were run. The procedure was exactly as in the foregoing except that the flasks were removed at the intervals noted.

Table II—Relative Rates of Saponification in Ethyl and Butyl Alcohols

Time, Min.	5	10	15	20	25	30	40	45	50	60
Cod-liver Oil:										
E	140.1	...	153.8	...	...	152.7	..	180.6	...	185.7
B	190.2	...	190.4	190.3	190.3	...	..	...	...	...
Castor Oil:										
E	171.1	173.3	...	...	178.0	...	...	...	177.3	177.7
B	147.5	166.0	177.5	...	180.4	180.5	...	...	...	...
Spermaceti:										
E	...	56.5	...	...	113.2	...	..	82.7	115.3	115.3
B	104.7	105.9	109.8	...	126.7	126.7	..	...	...	...

It appears from these results that the saponification of cod-liver oil is complete in 5 min. in normal butyl alcohol but requires considerably more time in ethyl. Castor oil is saponified rapidly in both, while spermaceti is acted on less rapidly in both but much more rapidly in butyl than in ethyl.

CONCLUSION

Normal butyl alcohol is found to be superior to ethyl as a medium for quantitative saponification, as by its use satisfactory results are more readily obtained and special precautions are less often required.

A NEW METHOD FOR THE DETERMINATION OF SULFUR IN OILS[1]

By C. E. Waters

Bureau of Standards, Washington, D. C.

Received November 6, 1919

It is well known that crude petroleum from whatever source contains more or less sulfur in combination. The lubricating oils and other products obtained from the crude oil must also contain sulfur unless special methods of refining are applied. In addition to their original sulfur content, the oils may be contaminated by sulfonic acids[2] which are formed when the oils are treated with concentrated sulfuric acid during refining, and are not afterwards completely washed out.

Little is known about the relation between the sulfur content and certain of the properties of oils. The chief reason for this may be the inconvenience, if not also the inaccuracy, of nearly every method that has been suggested for the determination of this element. Specifications have little to say about it. A limiting value may be set for fuel oils on account of the corrosive effect of the products of combustion. Transformer oils must contain a minimum amount. The test with polished copper, which is frequently called for, may be regarded as a demand for a low content of sulfur, because it is commonly believed that this element will always blacken the metal,[1] and will, therefore, have a bad effect upon bearings.

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[1] Published by permission of the Director of the Bureau of Standards.

[2] Although spoken of as sulfonic acids, it is certain that they are, at least in part, the acid esters of sulfuric acid and, therefore, analogous to ethyl sulfuric acid. The true sulfonic acids cannot be hydrolyzed by digestion with mineral acids, but this action takes place readily with the esters, and the sulfuric acid is recovered. When true sulfonic acids, *e. g.*, benzenesulfonic acid, is broken down by regulated fusion with caustic alkali, the sulfite of the metal is formed A heavy red oil (from F. R. Baxter, Vacuum Oil Co.), known to contain "sulfonic acids," gave no reaction for sulfuric acid when digested with water, but a slight reaction when so treated with 1 : 1 hydrochloric acid. When sealed up with concentrated hydrochloric acid and heated inside a steam bath, it gave a strong reaction for sulfuric acid.

It is believed by some that "sulfur compounds" are the cause of the tendency of an oil to form emulsions with water.[2] This may be true if the compounds are "sulfonic acids."

It is well established that when an oil is heated in the air, the amount of asphaltic matter formed is increased by the presence of sulfur or sulfur dioxide.[3] It might also be expected that the "gumming" of an oil at ordinary temperatures will be affected by the presence of sulfur, unless it is due only to the loss of the more volatile constituents.

Sulfur is known to have a beneficial effect in the flotation of certain ores. This is referred to by E. C. Bingham[4] in discussing the reason for using it in cutting oils.

For about eleven years the author has worked, as opportunity offered, on a variety of methods for the determination of sulfur in petroleum oils. Not only the published methods but others that seemed promising were tried. Because the subject first came up in connection with transformer oils, the aim was to find an accurate and convenient method which could be used with at least 2 or 3 g. of oil. With the bomb calorimeter, one gram is all that can be burned completely. No more can be used when the oil is burned in a bottle of oxygen, according to the Graefe method, and even much less is almost certain to cause the bursting of Carius tubes. Other methods are too slow, inconvenient, dangerous, or unreliable. Even combustion in the bomb is believed to give slightly low results. Analyses made by the method described in this paper appear to prove this.

Some years ago it was found that concordant results for sulfur could be obtained by digesting the oil in a Kjeldahl flask with concentrated nitric acid. From time to time a little crystallized potassium permanganate was added. This quickly decomposed, the acid became filled with suspended manganese peroxide, and the oxidation was materially hastened. Permanganate was chosen rather than chlorate because of this formation of a solid peroxide, instead of gaseous oxides. Chlorate was used about this time by Gilpin and Schneeberger[5] in the analysis of fractions from California crudes. They obtained results that checked those by the Sauer method. Although digestion with nitric acid usually gives concordant figures, some of our recent work shows that a considerable part of the sulfur may be lost.

In 1911 the author worked out a procedure for the determination of total sulfur in rubber goods.[1] The rubber is first decomposed to a considerable extent by digesting it with concentrated nitric acid saturated with bromine. It is then completely burned by heating with a mixture of soda and saltpeter. The decomposition of oils by means of nitric acid and permanganate requires many hours, and the disappearance of the oily drops does not indicate with certainty the end of the reaction. For this reason it was decided to try the method used for rubber, though with little hope of success. A topped Mexican crude, in which the sulfur content was found by nitric acid digestion to be 2.21, 2.17, and 2.27 per cent, was used. Three analyses by the method for rubber gave 4.06, 4.03, and 4.05 per cent of sulfur. Similar data from another oil showed that more than half of the sulfur was lost by the nitric acid method. This loss was traced to the formation of a nitro-compound which contained considerable sulfur. This nitro-compound was thrown down when the digestion flask was washed out after all of the oil had, apparently, been decomposed. It was soluble to some extent in water and dilute nitric acid, could be extracted but incompletely by ether, and was slightly volatile with water vapor when heated on the steam bath. Although a clear yellow oil, it formed a very dark brown salt when dissolved in a solution of soda. The success of the new method for the determination of sulfur appears to depend upon the formation of nitro-compounds which react with soda, and are therefore not driven off during the subsequent fusion with soda and saltpeter. An oil which yielded 1.83 per cent of sulfur showed only 1.37 per cent when the preliminary treatment with nitric acid and bromine was omitted.

DESCRIPTION OF METHOD

Weigh from 0.5 to 1.5 g. of oil into a 100 cc. porcelain crucible, add 5 cc. of concentrated nitric acid saturated with bromine, and at once cover with a watch glass. If there is danger of losing sulfur, as with a vulcanized oil or a rather volatile one, each sample should be treated with acid as soon as it is weighed out and not left until the series of weighings is finished. It is best to weigh such oils in a covered crucible. Place on the steam bath, but not in direct contact with the steam, and digest for 30 min. or more, with an occasional gentle swirling of the crucible. If the mixture does not threaten to foam up to the cover, the crucible may now be heated directly by the steam for 2 or 3 hrs.

Remove the crucible from the bath and, when its contents are cold, raise the watch glass slightly and add cautiously in small portions, 10 or 12 g. of anhydrous sodium carbonate. This is conveniently measured in a 15 cc. crucible, rather than weighed. The first portions of the soda usually remain on top of the oily layer, so that the crucible must be tilted or swirled slightly to start the reaction. When about half of the soda has been added it is safe to rinse the watch glass with 1 or 2 cc. of water and remove it permanently. Add the rest of the soda and thoroughly mix the contents of the crucible with a stout glass rod (3 mm.

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[1] This is not true. A topped Mexican crude, which contained 4.05 per cent of sulfur, barely tarnished a strip of copper which was heated in it for 2 hrs. at 290° to 295° C. At room temperature there was barely any action in several days.

[2] C. W. Stratford, private communication. A few experiments in collaboration with G. A. Kramer indicate that a high content of sulfur does not always cause an oil to emulsify readily.

[3] Holde and Eickmann, *Mitt. kgl. Materialprufungsamt*, **1907**, 145; *Z. angew. Chem.*, **20** (1907), 1263, 1923; Waters, Bureau of Standards, *Tech. Paper* **4** (1911), 9; THIS JOURNAL, **3** (1911), 814; Southcombe, *J. Soc. Chem. Ind.*, **30** (1911), 261.

[4] Unpublished paper.

[5] *Am. Chem. J.*, **50** (1913) 66.

[1] Waters and Tuttle, Bureau of Standards, *Scientific Paper* **174**; THIS JOURNAL, **3** (1911), 734.

thick and about 12 cm. long). The resulting pasty mass is spread around on the sides and one-half to two-thirds of the way to the top. If the right amount of water is used the mass will adhere to the crucible. The rod is not removed. Dry on the steam bath, or in an air bath at about 100° C., place the crucible in an inclined position on a wire triangle and start the ignition over a low flame. When more than a gram of oil has been taken, there is a tendency for it to burn too briskly, but this is controllable by judicious use of the stirring rod, which scrapes the burning portion away from the rest. When part of the mass is burned white, a fresh portion is worked into it, and so on until all of the organic matter is destroyed. It is necessary to hold the edge of the crucible with tongs. Towards the last half of the operation the flame should be increased somewhat, but it is never necessary to heat the crucible to redness. With care a crucible can be used for at least ten or twelve analyses.

According to the amount of oil taken the mixture of sodium salts resulting from the combustion varies from pasty to granular. After cooling, place the crucible on its side in a 400 cc. beaker with about 150 cc. of water. Cover and digest on the steam bath. When the salts have dissolved, remove and rinse out the crucible. Filter the solution to remove specks of carbon chips from the glass rod, etc. Acidify with concentrated hydrochloric acid, using Congo red paper as indicator, and add about 2 cc. of acid in excess. The reaction proceeds more safely if nearly the required amount of acid is placed in a covered beaker and the solution filtered directly into it. The total amount of carbonate and nitrite to be neutralized will depend upon how much oil was taken. Heat the acidified solution on the steam bath, add 10 cc. of a 10 per cent solution of barium chloride and digest until the sulfate is all thrown down. If time permits, the barium sulfate should be allowed to stand over night before it is filtered off, ignited, and weighed.

A blank should be run with the reagents. In doing this an ignition is to be made just as if oil were present, because the flame may contain some sulfur. The reagents used in making the analyses upon which this method is based gave only traces of barium sulfate when mixed in the usual amounts without ignition; including this, the correction amounted to 0.03 per cent of sulfur, based on one gram of oil. Most of this barium sulfate came down over night.

In this work, as in the routine analysis of rubber goods in this laboratory, a petroleum ether flame is used for the ignition. Gasoline can be used, but it is necessary to set the vessel which contains it in a beaker of warm water. A simple gasoline gas generator was described in 1913.[1] In place of the special form there described, a gas-washing bottle, containing a layer of glass beads to break up the bubbles, or even a wide-mouthed bottle with a good cork and two glass tubes, one of which extends to the bottom, can be used. A current of air blown through the petroleum ether carries with it enough vapor to supply a small burner of the Meker type. When first lighted the flame is apt to be smoky, but this ceases when the ether becomes chilled by evaporation. The smokiness is no great drawback because at the start of the ignition the flame should be so low as not to touch the crucible.

It is a merit of the method that a considerable number of determinations can be started and completed at the same time. Individual attention is needed chiefly during the ignition, which takes from 15 to 25 min. Rubber is so completely broken down that much less time is required. With oil there is so little change that most of it is driven off in clouds of vapor, and it seems that only a small part of the sulfur could possibly be held back. But the concordance of the results is strong, presumptive evidence that there is very little or no loss. In all, twelve oils were analyzed and found to contain from 0.29 to 4.05 per cent of sulfur. In three cases duplicate analyses differed by 0.06, 0.05, and 0.04 per cent; twice the differences were 0.03 and 0.01 per cent; and twice exact agreement was obtained. In three instances the discrepancy was 0.02 per cent.

In some recent work done in coöperation with the sub-committee on sulfur, Committee D-2, American Society for Testing Materials, three oils were analyzed in nine laboratories, including that of the author. The results varied widely and, in every case but one, the method just described gave the highest figures. The other members of the sub-committee used various methods: the bomb calorimeter, Sauer's method, Conradson's (burning in a lamp), and burning in oxygen at atmospheric pressure (Graefe's method). Table I gives the highest and lowest figures[1] obtained in the other laboratories, by all the methods. The results of all the analyses by the new procedure are also given. These have been corrected, by small amounts, for the sulfur in the reagents, in the flame and in the air. The correction calculated for one gram of oil was 0.03 per cent.

TABLE I—COMPARISON OF RESULTS OBTAINED BY DIFFERENT METHODS

	PERCENTAGES OF SULFUR						
OIL	By Other Laboratories	By New Method					
Mexican (topped crude with same vol. mineral seal)	1.27 to 1.98			1.83	1.82		
Vulcanized 300 oil	0.80 to 1.22	1.31	1.37	1.32	1.32	1.33	Av. 1.33
Heavy red oil	0.39 to 0.53	0.56	0.55	0.59	0.58		Av. 0.57

The vulcanized oil contained much hydrogen sulfide and probably also free sulfur. The heavy red oil contained "sulfonic acids."

In view of all the above figures it seems fair to claim that the present method is sufficiently accurate for the analysis of oils no more volatile than the "300" oils. It has not yet been applied to kerosene or gasoline. The analysis of six fuel oils, both light and heavy, which were obtained for this purpose from the Bureau of Mines Experiment Station, Pittsburgh, Pa., has been begun. The few results so far obtained seem to show that the new method gives somewhat higher sulfur than the bomb calorimeter.

It is admitted that the conditions under which the barium sulfate is precipitated are far from ideal, because of the occlusion of sodium salts. Of these the sulfate tends to low results, while the nitrate has the opposite effect. Only by chance will these errors cancel one another.[1] A few determinations made with double the usual amounts of reagents seem to show that the net error due to occlusion is small.

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[1] THIS JOURNAL, 5 (1913), 853.

[1] Taken from the report of the Chairman, F. R. Baxter, Vacuum Oil Co., and used by his permission.

The present paper is a preliminary one, and it is intended to publish a more detailed discussion of the whole subject later on.

SUMMARY

The desirability of investigating the possible effect of sulfur compounds on the properties of lubricating oils is pointed out.

The disadvantages of the methods now in general use for the determination of sulfur are indicated.

A new procedure, which gives results at least as accurate as those by the bomb calorimeter, is described.

DETERMINATION OF MINUTE QUANTITIES OF OIL IN SULFUR

By L. S. Bushnell and H. Smith Clark
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Received November 25, 1919

The presence of very small amounts of oil in sulfur is objected to by manufacturers of certain sulfur products. The sulfur may contain carbonaceous residues from burned oil, and the method here described is not intended to include these.

The estimation of oil by simple extraction as ordinarily made with a volatile solvent—such as sulfuric ether or petroleum ether—will not suffice in the case of sulfur, because, while the sulfur is only slightly soluble, there is usually such a small amount of oil present (from 0.001 per cent to 0.32 per cent, or more) that the extract contains considerably more sulfur than oil. In this method extraction is made as usual, and the solvent purified from sulfur by boiling it in a Wiley continuous extractor in which has been placed a roll of copper foil.

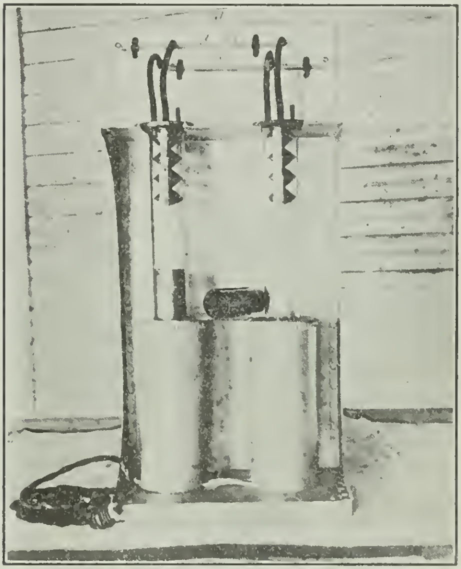
APPARATUS

A sheet of copper foil 4 in. × 15 in. is rolled up in such fashion that no two points of its surface come in contact. It is desirable that the copper sheet be rolled uniformly so that there will be a space of about three-sixteenths inch between any one turn of the roll and the next turn. The sheet may be cut so that at one corner a tab three-eighths inch square projects. A hole is punched in this tab so that the coil may be lifted from the Wiley tube with a wire hook. The end with this tab should be rolled first, and the tab project from one end of the coil.

A 100 cc. volumetric flask; a thin glass beaker, tall form, without lip, 300 cc. capacity; and a Wiley continuous extractor, without crucible or thimble, complete the required apparatus.

PROCEDURE

Fifty grams of the pulverized sulfur (or a smaller quantity, if the oil content is known to be high) are weighed and transferred to the 100 cc. flask. On this are poured about 50 cc. of redistilled petroleum ether; the flask is thoroughly shaken every half hour for several hours, and allowed to settle. The petroleum ether is decanted through a filter into a Wiley tube, and a second smaller quantity of the solvent is added to the flask, shaken, settled, and filtered, as before. The washing is continued in this way until the sulfur and the filter paper are free of oil, and the Wiley tube contains about 175 cc. of solvent, or enough to fill the tube above the top of the copper roll or coil.



The copper coil is cleaned with dilute nitric acid, washed with water, then with alcohol, dried with ether, and placed in the Wiley tube. The petroleum ether is then boiled until all of the sulfur has been deposited on the copper as copper sulfide.

The solvent is transferred to the tall beaker, filtering if necessary to eliminate the copper sulfide, which will doubtless partially flake off. The coil, the Wiley tube, and the filter are washed with small quantities of petroleum ether, the combined filtrate and washings gently evaporated to dryness at very low heat, and the residue weighed.

NOTE ON THE SOLUBILITY OF BENZIDINE SULFATE IN WATER

By C. S. Bisson and A. W. Christie
University of California, Berkeley, California
Received September 9, 1919

One of the methods for the determination of sulfates which has found considerable application consists in precipitation as benzidine sulfate, which may be quantitatively titrated with standard alkali or potassium permanganate. In most of the articles describing such methods, the benzidine sulfate is said to be insoluble in water. A review of the literature failed to reveal any definite data on its solubility except a statement by Muller[1] which gives it as from 0.01 to 0.03 per cent at 25° C. We have determined its solubility at different temperatures by agitating an excess of benzidine sulfate with pure water in a constant temperature thermostat.

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[1] Allen and Johnston, *J. Am. Chem. Soc.*, **32** (1910), 588; Johnston and Adams, *Ibid.*, **33** (1911), 829.

The benzidine sulfate was prepared by adding an excess of dilute sulfuric acid to an aqueous solution of Kahlbaum's benzidine. The precipitated sulfate was filtered and washed with distilled water till free of acid. From 3 to 5 g. were placed in a 500 cc. Pyrex flask containing pure water and the flask immersed in a thermostat which was regulated to 0.5° C. The contents of the flask were continually agitated by a revolving glass stirrer. After a specified number of days the solution was removed and immediately filtered, the first 20 cc. of filtrate being discarded. Solubility determinations were made at 0°, 25°, 50°, and 80° C.

Two methods for determining the solubility of the benzidine sulfate were used. One method consisted in evaporating a measured volume of 100 or 200 cc. to dryness in a platinum dish on the steam bath. The residue was dried at 100° C., cooled in a desiccator, and weighed. The other method consisted in titrating a measured volume of the solution with 0.05 *N* potassium permanganate after the addition of 5 per cent of sulfuric acid. The latter method is described in detail elsewhere.[2]

The solubility of benzidine sulfate in water as determined by the above methods is given in the accompanying table.

SOLUBILITY OF BENZIDINE SULFATE IN WATER AT VARIOUS TEMPERATURES

Temperature ° C.	Determination By Weight G. per Liter	Determination By Titration G. per Liter
0	0.049	0.048
25	0.098	0.096
50	0.141	0.149
80	0.290	0.252

The two methods gave concordant results at all the temperatures except 80° C. The solutions for the determination of solubility at 0° and 25° C. were stirred in the thermostat for four days. Those at 50° and 80° C. remained in the thermostat only 24 hrs., since it was found that after several days the solutions became badly discolored, indicating that the benzidine sulfate had undergone decomposition. The solution obtained at 80° C. was slightly discolored even after 24 hrs., as was also the residue obtained on evaporation. This is probably due to the partial oxidation of the benzidine at the higher temperature, as evidenced by the low figure for solubility obtained by titration. The residue obtained from the 50° solution showed only a very slight discoloration and the results may be considered to give the approximate solubility at this temperature.

From a consideration of these results it is evident that in washing the benzidine sulfate in a quantitative determination of sulfate, the minimum amount of cold water should be used.

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[1] *Ber.*, **35** (1902), 1587.

[2] A. W. Christie and C. S. Bisson, THIS JOURNAL, **12** (1920), 171.

LABORATORY AND PLANT

A CONVENIENT METHOD FOR THE DETERMINATION OF WATER IN PETROLEUM AND OTHER ORGANIC EMULSIONS[1]

By E. W. Dean and D. D. Stark

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Received January 15, 1920

INTRODUCTION

One of the problems frequently confronting the petroleum chemist is the determination of emulsified water. Numerous methods have been devised, several of which have been described in a previous publication[2] issued by the Bureau of Mines. Allen and Jacobs discuss in that paper the advantages and limitations of various types of procedure and recommend as most desirable the scheme of distilling in a special electrically heated still. This type of still involves heating the entire outer surface of a 250 cc. distilling flask and its use permits the "breaking" of troublesome froth that is usually formed when a viscous petroleum emulsion is heated. Certain difficulties in the construction and operation of this still have led to discontinuing its use in favor of the more common method of diluting the emulsion before distillation with a solvent immiscible with water. The present paper reports the work of the Bureau in modifying this latter method to obviate certain of its admitted disadvantages.

DISTILLATION IN THE PRESENCE OF AN IMMISCIBLE SOLVENT

There are various conditions under which it is desirable to determine water in petroleum emulsions and no one method is best in all cases. The method of gravity separation[1] is a convenient one and is satisfactorily reliable for emulsions that are not too viscous or that contain water in not too fine a state of subdivision. For the estimation of extremely small percentages of water, in such products as transformer oils, special methods are necessary which are too delicate for ordinary needs. The distillation method is without doubt most generally applicable, highly reliable, and sufficiently accurate for all usual requirements. The use of a solvent not miscible with water offers several advantages, the most important of which is prevention of frothing. Its principle disadvantages concern details of operation, and the modified procedure described in the present paper has been found to obviate most of these difficulties.

This method of determining water has been used in a

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[1] Published by the permission of the Director of the U. S. Bureau of Mines.

[2] See Bibliography, p. 490.

[1] A common procedure is to place a measured volume of oil in a suitable graduated tube, dilute with naphtha, and spin in a centrifuge. The water is driven to the bottom of the graduated tube and its volume can be read directly.

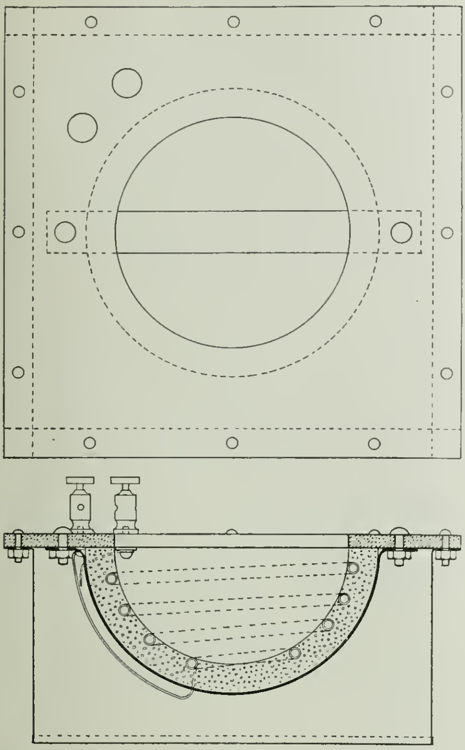

Fig. 1

variety of modifications and discussed in a number of published articles.[1] The following description covers the procedure commonly employed in petroleum laboratories.

A measured volume of the oil to be tested is placed in a glass or metal distilling flask and a suitable volume of solvent, generally petroleum naphtha of proper distilling range or a mixture of xylene and benzene, is added. The flask is connected with a condenser which delivers into some sort of a graduated receiver, heat is applied, and the distillation continued until the volume of water no longer increases. This volume is then read and the percentages of water in the original emulsion calculated. The principal objections and difficulties are:

1—Drops of water sometimes stick in the cool end of the condenser and are not easy to remove quantitatively.

2—The distillation requires a certain amount of attention and the distillate must be examined from time to time to determine when all the water has been driven over.

3—When emulsions of high-water content are tested it is sometimes necessary to add several successive portions of solvent to the contents of the distilling flask before all the water is driven over.

4—If a solvent such as xylene-benzene mixture is used there is an error due to the fact that an appreciable amount of water is dissolved in the upper layer of the distillate. Results must be corrected for this error or, preferably, the solvent must be saturated with water before adding it to the emulsion.

BUREAU OF MINES METHOD

The experimental work incident to the development of the method described in the present paper brought out a number of facts, which, though interesting, do not seem of sufficient general importance to warrant a detailed discussion. The results of the work are, therefore, reported in the form of a definite recommendation concerning apparatus and procedure. The specific recommendations are discussed in a subsequent portion of the paper. The following description covers the method as employed by the Bureau for all ordinary types of petroleum emulsions.

APPARATUS—The apparatus consists of a source of heat, a 500 cc. short-necked distilling flask, a special device combining the functions of distilling tube and receiver (hereafter referred to as "distilling tube receiver") and a condenser.

The source of heat may be an alcohol or gas burner, but the authors prefer a special type of electric heater, similar to that described by one of us in a previous article.[1] The form of the heater is, however, slightly different, as indicated in Fig. 1. The resistance elements now in service (with 110 volt alternating current) are composed of 23 ft. of No. 27 gauge nickel-chromium wire, having an approximate resistance of 72 ohms and an approximate capacity of 165 watts. These heaters are used without regulating rheostats, the capacity indicated having been found just sufficient to maintain the desired rate of distillation.

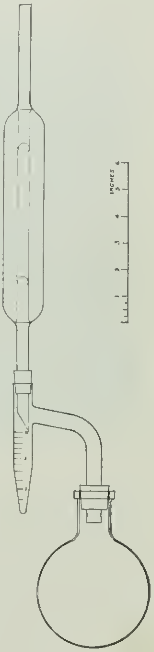

Fig. 2

The 500 cc. round-bottomed distilling flask is a readily obtainable stock article. The authors have found Pyrex flasks particularly satisfactory.

The "distilling tube receiver" (Fig. 2) is usually made[2] by attaching a proper side tube to a stock type of tapered graduated test-tube. It is the one essential part of the apparatus that must be specially constructed and the authors have been assured that the work is simple and that the article ought not to be expensive when put on the market.

The condenser, readily obtainable from chemical supply houses is about 15 in. long over all, and has an 8-in. sealed-on water jacket. The outside diameter of the inner tube is about $^{15}/_{32}$ inch. Before being put into service the tip should be ground diagonally, as indicated in the figure.

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[1] See Bibliography, p. 490.

[1] E. W. Dean, "A Convenient Electric Heater for Use in the Analytical Distillation of Gasoline," This Journal, **10** (1918), 823.

[2] The authors hereby acknowledge their indebtedness for aid in the design of this device to F. E. Donath, glass blower in the Pittsburgh Experiment Station of the Bureau of Mines.

The general method of assembling the glass parts of the apparatus is indicated diagrammatically in Fig. 2. Cork stoppers are used for the two junctions and if a good grade of cork is employed it is unnecessary to lute these joints.

For its own work the Bureau of Mines has developed a 4-unit electrically heated installation which has proven exceedingly satisfactory. A photograph of this installation is shown in Fig. 3.[1]

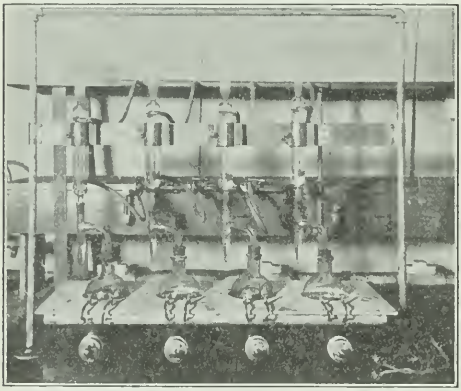

Fig. 3

IMMISCIBLE SOLVENT—The authors have found the most satisfactory solvent to be a so-called cleaner's naphtha derived from petroleum. The following specification covers the distillation range of this product, as determined by the standard method recommended by the Bureau:[2]

5 per cent mark not below 90° C. (194° F.)
nor above 100° C. (212° F.)
90 per cent mark not above 195° C. (383° F.)

A mixture of 80 per cent of commercial xylene and 20 per cent of commercial (so-called 90 per cent) benzene has also been found satisfactory. This mixture should not be saturated with water before using.[3]

PROCEDURE—Place 100 cc. of the emulsion to be tested in a graduate and measure out 100 cc. of solvent. Pour the emulsion into the 500 cc. flask, letting drain for a minute or two. Then wash all the emulsion out of the graduated cylinder, using successive portions of the measured 100 cc. of solvent. Drop a "boiling stone" (a bit of unglazed porcelain) into the flask. Connect with the distilling tube receiver and the condenser, making sure that the ground tip of the latter is placed so that drops of the condensate must fall into the receiving graduate and not into the side tube, and making sure that the position of the diagonally ground tip is approximately as indicated in Fig. 2.[1]

Apply heat until the distillation is proceeding at the rate of 2 to 4 drops per second, observing the rate of fall from the ground tip of the condenser, and establish the degree of heat necessary to maintain this rate. Allow the distillation to continue until all droplets of water in the flask, the distillation tube, and the condenser have disappeared. This usually takes less than an hour and in routine work it is convenient to start the distillation, let it run for an hour, then come back and make the final readings. In case a ring of droplets of water is observed in the condenser tube the rate of distillation should be increased for a few minutes so that the vapor level on the condenser tube is raised slightly, thereby sweeping off the water. The rate of distillation can be increased by applying more heat, or by placing an insulating shield of asbestos paper over the flask. The formation of a ring of water generally does not occur if the condenser tube is clean.

The heat is then turned off and the distilling flask disconnected. (It is not necessary to wait until it cools provided care is taken not to let the escaping vapor ignite.) A drop of water sometimes hangs on the ground tip of the condenser; this, however, practically always falls off when the graduated receiver is detached from the condenser.

The volume of water collected in the graduated receiver is then read, taking care that the tube is held in a vertical position. The receiver is emptied and dried, and is ready for another determination. The flask is usually set aside to cool and a previously cleaned and dried one used for the next determination.

DISCUSSION OF DETAILS OF THE ABOVE PROCEDURE

SOURCE OF HEAT—The authors have tried electric heaters of the design described, and gas burners.[2] The former are by far the more satisfactory but are not essential to the accuracy of the method. Perfectly satisfactory results were obtained with gas burners but a little more attention was required. It is possible that the easily obtainable electric hot plate would serve, although in this case it probably would be desirable to employ a flat-bottomed flask.

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[1] The authors acknowledge their indebtedness to W. A. Jacobs, Assistant Chemical Engineer, and Harry Buss, Chief Instrument Maker, of the Pittsburgh Experiment Station of the Bureau, for the design and construction of this highly satisfactory installation.

[2] E. W. Dean, "Motor Gasoline, Properties, Laboratory Methods of Testing, and Practical Specifications," Bureau of Mines, *Technical Paper* **214** (1919), 18.

[3] The commercial hydrocarbon products derived from the distillation of coal appear to dissolve water in slight but appreciable degree. With the original distillation method the full amount of solvent was distilled and collected in the receiver in contact with the water layer. A convenient means of compensating for the amount of water necessarily dissolved was to saturate the solvent before using. With the modified method herein described the volume of solvent in contact with water in the receiving graduate is of the order of 10 cc. or less and the error introduced through solution of water by this quantity is negligible. If the solvent is saturated before using, the amount of water collected in the receiver is always in excess of that actually contained by the oil tested.

[1] When determinations are made in an atmosphere of high humidity it is advisable to take certain precautions designed to prevent any extraneous water from entering the receiving graduate. A protecting shield such as a circle of blotting paper may be slipped over the condenser tube and held in place between the cooling jacket and the cork stopper connecting the condenser and distilling tube receiver. This obviates any possibility of water dripping from the condenser and passing through a cork that is not absolutely tight. Another more essential precaution for operations in an atmosphere of high humidity is to place a loose plug of absorbent cotton in the upper (open) end of the condenser tube, thereby preventing free access of air which might be deprived of moisture with a resulting increase in the volume of water apparently separated from the oil. A properly trapped calcium chloride tube can, of course, be used instead of a plug of cotton, but the latter is regarded as adequate protection for all cases except those requiring extreme accuracy.

[2] If a flame heater is employed it seems advisable to have the flask bottom protected by a piece of wire gauze.

FLASK—The authors generally employ a short-neck, round-bottom, 500 cc. Pyrex glass flask. None of these particular details are, however, essential. The size of the flask, in particular, may be varied in case the total volume of the charge of emulsion and solvent is notably more or less than 200 cc. Metal flasks can, if desired, be substituted for glass, and the scheme of using flat-bottomed distilling vessels has already received mention.

DISTILLING TUBE RECEIVER—Numerous designs for this device have been tried and the type recommended has proved most satisfactory. For certain types of work it can undoubtedly be modified to advantage and occasion has already arisen in the Bureau laboratories to substitute a plain tube with a glass stopcock. This modification permitted the handling of emulsions containing large percentages of water, the water being drawn off through the cock into a measuring cylinder from time to time. It is entirely possible that other modifications may be desirable under conditions that may be encountered and the present device is recommended as simply the most convenient type that has been used with the types of emulsions that are generally tested in the Bureau laboratories.

CONDENSER—The type of condenser described was selected more or less by accident but has been found entirely satisfactory.

SOLVENT—A considerable variety of solvents have been tried and the two recommended above were found most satisfactory. The desirable properties are those which insure "smoothness" in distillation and a vapor temperature slightly above the boiling point of water. The solvent must have a certain percentage of constituents boiling below 100° C., but this percentage must not be too great. For instance, ordinary motor gasoline, with about 20 per cent boiling below 100° C., was notably less satisfactory than the special naphtha that is described in a previous connection. The final boiling point of the solvent apparently should not be too high as was evidenced by the fact that unsatisfactory results were obtained by the use of a solvent made by blending kerosene with ordinary motor gasoline in sufficient proportion to reduce the portion distilling below 100° C. to between 5 per cent and 10 per cent.

The solvent must be immiscible with water but should, under ordinary conditions at least, be miscible with the oil or other non-aqueous constituent of the emulsion. The application of this latter requirement is illustrated later when the results of tests on coal tar are discussed. The degree of solubility of water in the solvent is of some importance, though such errors are minimized by the fact that the quantity of non-aqueous distillate in the receiving tube is never more than 10 or 12 cc. Water is almost perfectly insoluble in the petroleum naphtha. It is probable, however, that many laboratories will find it more convenient to prepare the xylene-benzene mixture than to obtain a special grade of petroleum naphtha. Water is slightly soluble in coal-tar distillates and in addition there is sometimes a tendency for the distillate to be cloudy, due to the holding back of minute particles of water. Permitting this cloud to settle has never, however, added as much as 0.01 cc. to the volume of the water layer.

PROCEDURE—The use of a charge of 100 cc. of emulsion and 100 cc. of solvent has proved satisfactory for oils containing between 0.5 and 10.0 per cent of water. If an accurate determination of water content of less than 0.5 per cent is desired it is necessary to use 200 cc. or more of both emulsion and solvent, employing, of course, a correspondingly larger distilling flask. If the emulsion to be tested contains more than 10 per cent of water the quantity taken should be some suitable fraction of 100 cc. According to the authors' experience it has not seemed necessary to change either the quantity of solvent or the size of the distilling flask when this method of handling emulsions of high water content is used.

The procedure recommended for measuring out the emulsion is a convenient one but not essential to the method. In some cases a pipette can probably be used to advantage. The use of a boiling stone has proved necessary and a number of determinations have been spoiled through failure to remember this detail. If it is omitted boiling sometimes begins explosively and oil is blown out through the top of the condenser.

RELIABILITY AND ACCURACY OF METHOD

The method has been tried with a number of emulsions prepared by mixing known amounts of water with anhydrous oils. Results have almost invariably checked the theoretical water content within ± 0.1 cc., which apparently represents the normal magnitude of error. The applicability of the method for the separation of water from refractory emulsions has been questioned and tests have been made to settle this point. Water was determined according to the procedure described. The flasks were allowed to cool somewhat, then connected with an ordinary distilling tube and condenser and the distillation continued until a vapor temperature of 250° C. was reached. In no case was any additional water separated or observed, thereby indicating that distillation at the temperature existing in the presence of the solvent was adequate to "break" the emulsion.

APPLICABILITY TO SUBSTANCES OTHER THAN PETROLEUM

The method was tried with several samples of grease and yielded results that were considered highly satisfactory by the operator who had had considerable experience with the conventional methods for determining the water content of greases. It was also tried with several samples of coal tar. The naphtha solvent proved useless for this type of emulsion, the tars in question being quantitatively insoluble in petroleum distillate. The xylene-benzene solvent, however, was satisfactory and the results of the determinations were apparently as reliable as when petroleum emulsions were tested.[1]

The authors believe that the method herein described is applicable to a wide variety of organic emulsions, possibly solid as well as liquid, and recommend its trial in all laboratories not fully satisfied with the methods at present in use. While it is not believed that results may necessarily be more accurate than those now obtainable, an increase in convenience and rapidity is anticipated.

PREVIOUS WORK ALONG SIMILAR LINES

On account of the simplicity of the modified method the authors have found it difficult to believe that their work could be new. The literature has been searched diligently, however, and it has been found that practically all the distillation methods for water determination have involved the use of apparatus of the conventional type and arrangement. The methods of Besson and Gray approach most closely the procedure recommended in the present paper. The basic idea of the authors' method was conceived after reading a description of the apparatus of Besson. Neither his method nor that of Gray is, however, believed to be as practical as that of the authors. The apparatus is not as simple and convenient and no attempt is apparently made to make the distillation continuous by refluxing the solvent into the flask.

SUMMARY

General experience has indicated that the method of distilling in the presence of an immiscible solvent is the most reliable and most generally satisfactory scheme of estimating the water content of organic emulsions, particularly petroleum emulsions.

The Pittsburgh Petroleum Laboratory of the Bureau of Mines has developed modifications of this method that add considerably to its convenience.

A description of the apparatus and procedure employed by the Bureau appears in the present paper.

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HEAT BALANCE OF A DISTILLATION PLANT FOR THE RECOVERY OF FATTY ACIDS FROM COTTONSEED FOOTS

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Received December 1, 1919

Some years ago the writer was engaged in development work along lines of fatty acid distillation. Before this could be undertaken it was necessary to know the value of the heat of vaporization of fatty acids under operating conditions, *i. e.*, at the temperature and reduced pressure usually employed in distillation. A search of the literature of this subject failed to yield the desired information and the determination of these values was, therefore, undertaken by the writer. The results are given here in the hope that they may be of value to the profession.

The heat of vaporization can be calculated from the vapor pressure curve of the fatty acids, and the latter can be determined in the laboratory. As a commercial fatty acid distillation plant was available, however, advantage was taken of this fact to make a large-scale determination. This was preferred, as it was thought that it would not be possible to reproduce working conditions on a laboratory scale. One of the most important of these factors is the effect of the pitch in the still bottom. As it accumulates it becomes necessary to raise the distillation temperature sometimes

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[1] Coal-tar emulsions are commonly believed to be more difficult to break up than petroleum emulsions and with the samples of tar tested particular care was taken to prove that no water remained after distillation in the presence of xylene-benzene mixture. The scheme of subsequently distilling the residue was employed and no water was discovered when the vapor temperature was carried as high as 250° C.

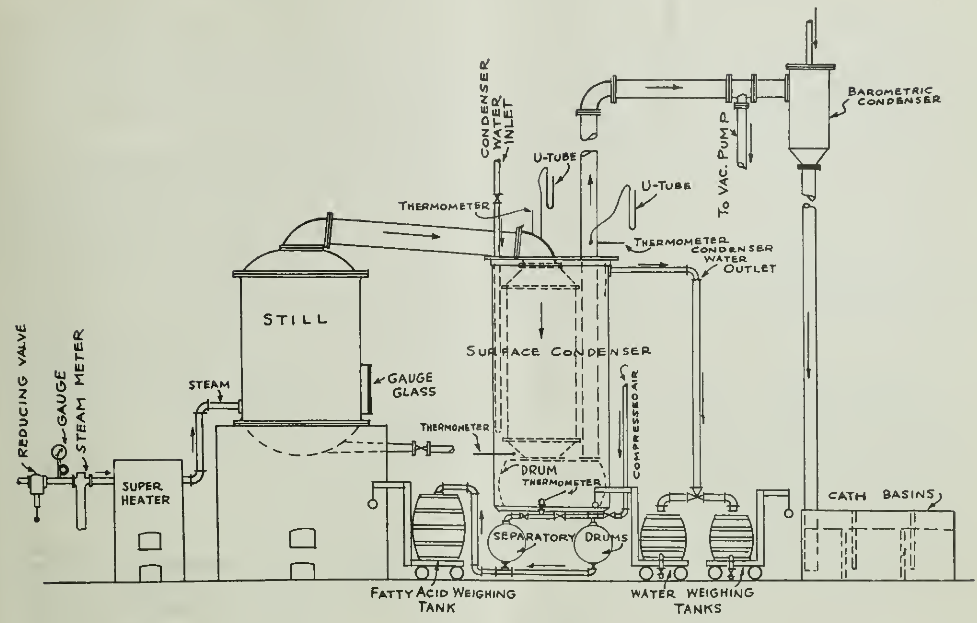

Diagram of Equipment

as much as seventy-five degrees or more. It was also believed that any variation in composition of the fatty acids or other factors would be averaged in a larger-scale determination.

The fatty acids were obtained from foots from the refining of crude cottonseed oil. The crude oil consists principally of a mixture of the glycerides of palmitic, linoleic and oleic acids containing also small quantities of glycerides of arachidic and possibly stearic acids.[1] In addition to these glycerides there are also present the glycerides of all these acids in various stages of decomposition.

Crude cottonseed oil is usually refined with caustic soda, whereby the partially and wholly decomposed glycerides are separated out as a soap (foots). This soap is only partially saponified and contains considerable quantities of neutral oil, together with most of the coloring, nitrogenous and mucilaginous matter that was present in the crude oil. The preponderant constituent of the foots is probably a soda soap of oleic acid, inasmuch as olein, the glyceride of oleic acid, is largely present in cottonseed oil and is most readily broken down. The composition of the foots will vary considerably, depending to a great extent on the amount of neutral oil retained in refining.

The foots may be killed and acidulated, *i. e.*, the saponification may be completed by boiling with sufficient alkali and the resulting soap treated with mineral acid to liberate the fatty acids; or the foots may be first treated with a mineral acid to free it from alkali, and then saponified by the Twitchell or other process to remove the remaining glycerol radicals. In either case the end result is a mixture of free fatty acids ready for the distillation process.

Two distillations were run on entirely different lots of fatty acids, since several months elapsed before the distillation plant could be spared for the second determination, and it was not practical under the existing conditions to store a portion of the first lot of stock for use in the second determination.

METHOD

The method employed in making the determination was as follows: The distillation plant was operated on fresh fatty acid stock, with no fatty acid or pitch left in the still from previous distillations. Before starting the tests, distillation was carried on until conditions were constant. A flying start and stop of the tests were used in a manner similar to that employed in making evaporative boiler tests. Thus, without interruption or disturbance of the distillation, tests were started and stopped immediately after emptying the condenser drums.

Measurements of all such quantities as were required to write a heat balance of the plant were made. Assistants were stationed at points where manual control was necessary. All readings were taken at 5-min. intervals.

The accompanying diagram gives an outline of the distillation plant employed. It consisted of a coal-fired still, supplied with superheated steam through a reducing valve and a separately fired superheater. This still was fed continuously so that the volume in the still was constant, the level in a gauge glass being carefully watched. The combined fatty acid vapor and superheated steam passed over from the still to a water-cooled tubular type of condenser. Here the fatty acids were condensed out and collected in a drum in the bottom of the condenser. At intervals the fatty acids were transferred to the separatory drums, whence, by means of compressed air, they were transferred to a scale tank for weighing. This scale tank is shown on the same floor level as the still. Actually, as a matter of convenience, it was placed on an upper floor, so that the fatty acid after weighing could be dropped into a storage tank on a lower level. Here entrained moisture was settled out and weighed. The distilled fatty acids were allowed to stand until laboratory tests showed that all the moisture had settled out.

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[1] Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," **2**, 5th Ed., p 197.

The steam passed over to a barometric condenser, and the fixed gases were taken care of by a vacuum pump. The barometric condenser discharged into a separatory catch basin, where the small quantity of entrained fatty acid was recovered by skimming.

The cooling water was carefully weighed, allowance being made for surface evaporation from the top of the open condenser and the scale tanks. This allowance was based on actual loss in evaporation of an open vessel immersed in the top of the condenser.

EXPERIMENTAL DATA ON FATTY ACID RECOVERY

	TEST A MARCH	TEST B MAY
Length of test	7 hrs.	7 hrs.
Average barometer corrected to 58.4° F.	29.62 in. Hg	29.10 in. Hg
Vacuum condenser vapor inlet corrected to 58.4° F.	24.13 in. Hg	24.24 in. Hg
Vacuum condenser vapor outlet corrected to 58.4° F.	25.17 in. Hg	24.68 in. Hg
Average temperature at vapor inlet	433.8° F.	445.5° F.
Average temperature at vapor outlet	141.9° F.	134.0° F.
Average temperature of stock into separatory drums	136.8° F.	131.9° F.
Average temperature of condensing water into condenser	33.6° F.	52.6° F.
Average temperature of condensing water out of condenser	123.1° F.	178.0° F.
Average temperature of condensing water, bottom of condenser	116.0° F.	118.5° F.
Total steam consumed	7229.0 lbs.	5901.0 lbs.
Total stock into separatory drums (after deducting settled water and moisture)	11077.0 lbs.	13091.0 lbs.
Total stock from 1st catch basin (after deducting moisture content)	3176.0 lbs.	2839.0 lbs.
Total stock from 2nd catch basin (after deducting moisture content)	286.0 lbs.	278.0 lbs.
Total stock (dry)	14539.0 lbs.	16208.0 lbs.
Average moisture content of stock.	0.713 per cent	0.4 per cent
Water carried with stock into separatory drums and settled out	538.0 lbs.	272.0 lbs.
Water present in stock into separatory drums as moisture	80.0 lbs.	53.0 lbs.
Water present in stock from catch basin	25.0 lbs.	12.0 lbs.
Total water carried over and present as moisture	643.0 lbs.	337.0 lbs.
Condensing water	57740.0 lbs.	36719.0 lbs.
Rate of evaporation of condensing water (lbs. per sq. ft. per hr.)	0.54 lb.	1.46 lbs.
Area from which evaporation took place	31.0 sq. ft.	31.0 sq. ft.
Area from which radiation took place	357.9 sq. ft.	357.9 sq. ft.
CALCULATED RESULTS		
Total heat to raise 1 lb. of stock from 32° F. to vapor under the test conditions	315.3 B. t. u.	308.2 B. t. u.
Heat to vaporize 1 lb. of stock under test conditions	130.5 B. t. u.	118.0 B. t. u.

To measure the vacuum, mercury U-gauges were placed at the inlet to the surface condenser and in the vapor pipe outlet, as close to the water surface as possible.

Temperatures were taken at these two points, also at the following points: the surface of water in surface condenser, water near bottom of condenser shell, cold water supply, and fatty acids at outlet of condenser drum. Wherever possible, thermometer wells were used, filled with appropriate liquids—at the vapor inlet, oil, on account of the high temperature, and elsewhere mercury.

The quantity of steam was determined by means of a specially calibrated Gebhart steam flow meter located between the reducing valve and the superheater. The quality of the steam was not determined. It was calculated that with a drop of pressure in the reducing valve, of some sixty odd pounds, the steam was practically dry and saturated.

With one exception, conditions were kept very close to the average, there being little or no variations. This exception was the temperature of the cooling water at the top of the condenser. This fluctuated somewhat more than was desirable, because of the difficulty in the water control and the large volume present in the condenser shell.

In the table are given the data of the two tests and the calculated results.

CALCULATION OF RESULTS

The method of arriving at the calculated results was as follows: A heat balance was struck. In this balance it was assumed that the steam as measured was dry and saturated. An error of perhaps one-half of one per cent enters here. It was further assumed that there was practically no condensation in the vapor pipe connecting the still with the condenser. As this pipe pitched toward the condenser, any condensation would be collected in the condenser drum. This pipe was 12 in. in diameter and 14 ft. long, and was insulated with very heavy magnesia covering. The heat loss was a negligible percentage of the total passing.

The temperature at the condenser inlet was assumed to be that of saturated fatty acid vapor, *i. e.*, it was assumed the fatty acid vapor carried no entrained liquid fatty acid and was not superheated. The very large diameter and height of the still precluded entrainment, and laboratory tests showed that at 28.25 in. to 29.5 in. of vacuum the boiling point is very close to 440° F. This checks very well with the actual large-scale tests where steam for distillation was used. As might be expected, somewhat lower temperatures were found.

The total heat in the superheated steam was obtained from the Molière chart and data published by Prof. C. C. Thomas.[1]

The heat lost by radiation from the condenser shell was calculated from the values in Kent's "Mechanical Engineers' Handbook."[2] The value used for the mean specific heat of the fatty acids was 0.46.

The heat balance as struck is given at top of next page.

The close agreements of the results is rather astonishing. There is a difference of only about 2 per cent in the values for total heat per pound of stock. However, the values for heat of vaporization differ by about

[1] *Trans. Am. Soc. Mech. Eng.*, **29** (1907).

[2] 1898 Ed., p. 536.

Total heat above 32° F. in the fatty acid distilled = Heat taken up by condensing water + Heat lost by evaporation of condensing water + Heat lost by radiation from condenser shell
− [Total heat above 32° F. of steam entering condenser − Total heat above 32° F. in steam leaving condenser − Heat above 32° in water carried over with stock into settling tank]
+ Heat to raise stock in condenser drum from 32° F to drum temperature + Heat to raise stock from catch basin from 32° F. to condenser temperature

Substituting the proper figures in this heat balance, and dividing by the quantity of fatty acid distilled, we find: Total heat above 32° F. per lb. of fatty acid distilled = 315.3 B. t. u. for Test A

Whence, on the assumptions before stated, we have: Heat of vaporization per lb. of fatty acid at 24.51 in. vacuum = 315.3−0.46 (433.8−32) = 130.5 B. t. u.

Similarly we find for Test B the values 308.2 B. t. u. and 118.0 B. t. u., but at 25.14 in. vacuum.

9 per cent. This discrepancy can be accounted for in two ways: Firstly, the stock was not the same in both cases. Undoubtedly, there was some difference in the mixtures being distilled, but unfortunately no chemical analyses were made to determine the difference; secondly, the two tests were made at somewhat different pressures and temperatures.

The heat of vaporization differs with temperature. If it did not the vapor pressure curve would be a straight line, and this we know is not the case. Probably the discrepancy is due to a combination of these two factors.

The writer desires to express his appreciation of the assistance rendered in this work by Messrs. S. B. Murdock, J. W. Bodman, and A. D. Whitby, and to thank the N. K. Fairbanks Company, through whose courtesy these figures are published.

NUMERICAL RELATION BETWEEN CELLS AND TREATMENTS IN EXTRACTION PROCESSES

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Received November 8, 1919

In a previous study of extraction processes[1] conducted at the U. S. Forest Products Laboratory, Madison, Wisconsin, it was found that no definite relation had ever been developed between the number of solvent treatments received by each charge of material and the number of cells or extractors required to furnish this number of treatments. It was also evident that the ideas in regard to such a relation were very much confused, and that the usual conception was the entirely unfounded one that for a certain number of treatments an equal number of cells was required or the same number plus one.[2] After it had been determined how many treatments in series were required for efficient extraction and how much time would be required for boiling, pumping, discharging, charging, etc., there was still no method by which it could be determined how many cells or extractors would be required by the process.

In the development of the numerical relation between the cells and the treatments it will be necessary to consider a general case covering all conditions; and this will require the use of terms and the assumption of conditions that may seem unusual or impractical to operators who have had experience with only one kind of extraction process and have used a peculiar set of terms for describing the various operations. On this account indulgence is requested from the readers who find unusual processes described in unusual terms, and they are asked to overlook these until the general principles become clear.

There is, of course, a definite relation between the number of cells and the number of treatments. It varies with different methods of manipulation, however, and several conditions of treatment must be known accurately before the relation can be developed. It is necessary to know the amount of time required for the operations performed on each charge other than the typical extraction operations, and this time must be known in terms of the typical extraction operations. These latter operations are:

1—The movement of solvent from one charge to another, from the last charge to storage or from the solvent tank to the first charge, which movements will be called "pumping" and designated by p.

2—The period of the actual solution action of the solvent on the charge, whether by standing, boiling, or agitating, which will be called "boiling" and designated by b. These typical operations are necessary parts of every discontinuous extraction process and may vary only in the time required for their fulfillment.[1] While there are only these two kinds of extraction operations, each may take place a variable number of times in a complete cycle of extractions. The non-extraction operations may vary widely in number, kind, and time required, and include charging and discharging the cells, or any preliminary or after-treatment performed on the charge while in the cells.

SIMULTANEOUS PUMPING

The simplest way to determine the relation between the number of treatments and the number of cells in terms of the time required for the various operations seems to be to use cut and try methods under several different sets of conditions and then to find the complete mathematical relation by inspection. This can be readily done by representing a series of extractions graphically. The easiest system to start with is one in which the pumping of all cells in action is done simultaneously. A series of extractions in four cells by this system can be represented as in Fig. 1.

In this method of representation the arrows indicate movement of the solvent or pumping; for instance, the first line of the diagram indicates simultaneous movement of solvent from cell 2 to cell 3, cell 3 to cell 4, and cell 4 to storage, while line 3 indicates simultaneous application of fresh solvent to cell 3, and movement of solvent from cell 3 to cell 4, and from cell 4 to cell 1. All cells are assumed to contain solvent except those with a double circle. Those indicated in line 2 as containing solvent but without solvent movement show the extraction or boiling period. By following this series of operations we find that a complete cycle has been finished in 16 lines and that line 17 is the same as line 1. During this cycle each cell receives 5 treatments and each batch of solvent is used 5 times. It will be noted that for a period of 3 boilings and 2 pumpings (indicated by braces) each cell stands idle so far as solvent action is concerned; this period is the time available for charging and discharging and for other preliminary or after-treatment of the charge. The relation between this idle period, n, the number of cells, c, and the number of treatments, t, in terms of the boiling period, b, and the pumping period, p, will now be worked out.[1] In the case just shown $n = 3b + 2p$ when $c = 4$ and $t = 5$.

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[1] This Journal, **9** (1917), 866.

[2] Kressmann, *Met. & Chem. Eng.*, **15** (1916), 78.

[1] As will be seen later, b may equal zero in some cases.

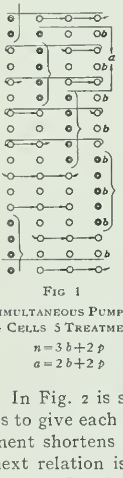

FIG 1

SIMULTANEOUS PUMPING 4 CELLS 5 TREATMENTS

$n = 3b+2p$

$a = 2b+2p$

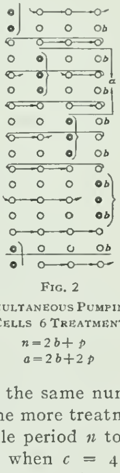

FIG. 2

SIMULTANEOUS PUMPING 4 CELLS 6 TREATMENTS

$n = 2b+p$

$a = 2b+2p$

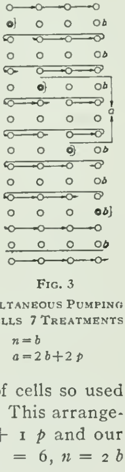

FIG. 3

SIMULTANEOUS PUMPING 4 CELLS 7 TREATMENTS

$n = b$

$a = 2b+2p$

In Fig. 2 is shown the same number of cells so used as to give each cell one more treatment. This arrangement shortens the idle period n to $2b + 1p$ and our next relation is that when $c = 4$ and $t = 6$, $n = 2b + p$. In the same way when one more treatment is obtained, the maximum possible in 4 cells, the time available for discharging, charging, etc., is reduced to a single boiling period. (See Fig. 3.)

Similar diagrams for various other numbers of cells and treatments were made and from them was prepared Table I in which the general relation between the factors c, t, n, b, and p becomes apparent.

From inspection of the table it is seen that n is composed of boiling periods equal in number to twice the number of cells minus the number of treatments, and of pumping periods always one less than the number of boiling periods, or

$$n = b(2c - t) + p(2c - t - 1) \text{ or } t = 2c - \frac{n+p}{b+p}.$$

It is suggested that more confidence in the table and in the formula derived from it will be produced if the reader will verify a few of the relations shown in the table by preparing diagrams similar to these given, but for different values of c or t. This procedure will also make it possible to follow the further similar developments more readily.

TABLE I—ALL CELLS PUMPED AT ONE TIME

CELLS c	TREATMENTS t	Time Available for Charging, Discharging, etc. n	Time between Discharges a
2	2	$2b + 1p$	$2b + 2p$
2	3	$1b$	$2b + 2p$
3	2	$4b + 3p$	$2b + 2p$
3	3	$3b + 2p$	$2b + 2p$
3	4	$2b + 1p$	$2b + 2p$
3	5	$1b$	$2b + 2p$
4	3	$5b + 4p$	$2b + 2p$
4	4	$4b + 3p$	$2b + 2p$
4	5	$3b + 2p$	$2b + 2p$
4	6	$2b + 1p$	$2b + 2p$
4	7	$1b$	$2b + 2p$
5	3	$7b + 6p$	$2b + 2p$

It should be noted further that in this method of operation, *viz.*, simultaneous pumping of all cells with a boiling period after every pumping period, the time elapsed between any similar operations on successive cells (which is the measure of the output of the system) is always the same, $2b + 2p$, whatever the number of cells or treatments. This period is indicated by a on the diagrams and shows the time elapsed between the beginning discharge of two consecutive cells.

CONTINUOUS EXTRACTION

It should be noticed here that these formulas are applicable also to continuous extraction. Continuous extraction is the same as the system of simultaneous pumping just described in which $b = 0$ and p is the period of time required for moving the liquid contents of one cell to the next or to storage. Under these conditions, $n = p(2c - t - 1)$ or $t = 2c - \frac{n+p}{p}$, and $a = 2p$.

SEPARATE PUMPING

It has been shown[1] that the method of pumping all cells simultaneously gives much less efficient extraction than pumping one cell at a time. It might possibly be thought that the pumping of only one cell at a time would take so much longer that in the case of a large number of cells it would lose more in time than would be gained in efficiency of extraction. Some very interesting comparative figures are obtained by developing the relations between c, t, n, etc., under this method of pumping. The method of representation of the extraction process is the same as in the other case, and the diagram, Fig. 4, shows that in an operation of 6 treatments in 4 cells $n = 2b + 4p$.

In this method there are two other variable time periods which are important and will also be studied; these are the average length of time each charge is boiled with each separate batch of solvent, designated by e, and the time elapsed between successive discharges, designated by a.

In this method of pumping the actual length of time each charge is boiled with each batch of solvent is not always the boiling period b only, but is variable. This is due to the fact that sometimes only one and

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[1] The letters used in designating the different variables are all shown either in this sentence or in the headings of Tables I and II.

[1] THIS JOURNAL, *Loc. cit.*

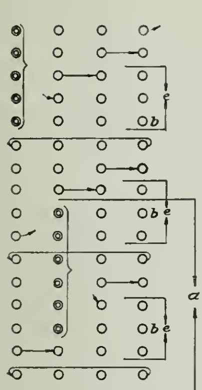

Fig. 4

Separate Pumping
4 Cells 6 Treatments
$n = 2b + 4p$
$a = 2b + 7p$
$e = b + 2p$

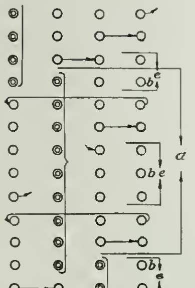

Fig. 5

Separate Pumping
4 Cells 5 Treatments
$n = 3b + 6p$
$a = 2b + 6p$
$e = b + {}^8/_5 p$

never more than two cells are in the pumping stage at one time, and as soon as one cell is pumped full it can immediately enter the boiling stage while the others are being pumped.

Table II—Each Cell Pumped Separately

Cells c	Treatments t	Time Available for Charging, Discharging, etc. n	Time between Discharges a	Average Single Boiling Period e
2	3	$1b$	$2b + 4p$	$b + 2/3\,p$
2	2	$2b + 2p$	$2b + 3p$	b
3	5	$1b$	$2b + 6p$	$b + 8/5\,p$
3	4	$2b + 3p$	$2b + 5p$	$b + p$
3	3	$3b + 4p$	$2b + 4p$	$b + 2/3\,p$
3	2	$4b + 5p$	$2b + 3p$	$b + 0\,p$
4	7	$1b$	$2b + 8p$	$b + 18/7\,p$
4	6	$2b + 4p$	$2b + 7p$	$b + 2p$
4	5	$3b + 6p$	$2b + 6p$	$b + 8/5\,p$
4	4	$4b + 8p$	$2b + 5p$	$b + p$
4	3		$2b + 4p$	
5	9	$1b$	$2b + 10p$	$b + 32/9\,p$
5	8	$2b + 5p$	$2b + 9p$	$b + 3p$
5	7	$3b + 8p$	$2b + 8p$	$b + 18/7\,p$
5	6	$4b + 11p$	$2b + 7p$	$b + 2p$

In the diagram showing 6 treatments in 4 cells, $e = b + 2p$ and $a = 2b + 7p$. In the next diagram, Fig. 5, showing 5 treatments in 4 cells the time n has increased to $3b + 6p$, $e = b + 8/5\,p$ and $a = 2b + 6p$.

In the same way diagrams have been prepared showing a wide variation in number of cells and number of treatments, and the resulting values for n, a, and e are given in Table II.

From this table the following formulas were developed[1] showing the various relations between c, t, n, a, and e.

Extractions in Which Every Charge Receives Two Treatments with Fresh Solvent

Simultaneous Pumping

$$n = (3c - t)\,b + (3c - t - 1)\,p$$

$$a = 3b + 3p$$

$$e = b$$

Separate Pumping

$$n = bc\,(3c - t - 1) - (3c - t\left(\frac{3c - t - 1}{3}\right)p \text{ when } t \text{ is multiple of 3}$$

$$n = bc\,(3c - t - 1) - \frac{(3c - t - 1)^2 - (3c - t - 1)}{3\,(3c - t)}\,p \text{ when } t \text{ is not multiple of 3}$$

$$a = 3b + (t + 2)\,p$$

$$e = b + (t/3 - 1)\,p \text{ when } t \text{ is multiple of 3}$$

$$e = b + \frac{(t-1)^3 - (t-1)}{3t^2}\,p, \text{ when } t \text{ is not multiple of 3}$$

$$n = (2c - t)b + c(2c - t - 5)p + (2t + 4)p \qquad (1)$$

$$a = 2b + (t + 1)p \qquad (2)$$

$$e = b + \frac{(t-1)^2}{2t}\,p \text{ (when } t \text{ is odd)} \qquad (3)$$

$$e = b + \frac{t - 2}{2}\,p \text{ (when } t \text{ is even)}$$

These formulas are of particular interest in showing that:

1—The extra time available for charging, discharging, etc., n, varies directly with the number of cells and inversely with the number of treatments obtained.

2—The length of time between successive discharges of material, a, which is really the reciprocal of the capacity of the system, is *not* influenced by the number of cells but is increased to a slight extent by an increased number of treatments.

3—The average actual time each charge is exposed to the boiling operation is not affected by the number of cells but varies to a slight extent with the number of treatments.

APPLICATION OF FORMULAS

Suppose for example it had been determined that a certain extraction process would require 6 treatments and that the pumping would take 10 min., the boiling 15 min., and the charging, discharging and solvent recovery 1.5 hrs. How many cells would be required for the process?

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[1] The development of similar formulas for extractions in which every charge receives two treatments with fresh solvent (This Journal, *Loc. cit.*) will not be given in detail but following are the formulas for this method of extraction which have been developed by the same method as the foregoing.

$$
\begin{aligned}
n &= b(2c - t) + p(2c - t - 1) \\
90 &= 15(2c - 6) + 10(2c - 6 - 1) \\
&= 30c - 90 + 20c - 70 \\
90 &= 50c - 160 \\
250 &= 50c \\
c &= 5
\end{aligned}
$$

If, however, n had been 60 min. instead of 90 min. the value of c would have come to 4.4; this would mean that either 5 cells would have to be used with a wait of 30 min. after charging before the first batch of solvent is ready to run on or else the time of boiling or of pumping would have to be lengthened so that 4 cells could do the work. If, for instance, 4 cells are to do the work, the boiling period must be lengthened to 25 min.

$$
\begin{aligned}
60 &= b(8 - 6) + 10(8 - 6 - 1) \\
60 &= 2b + 10 \\
b &= 25
\end{aligned}
$$

or the pumping period to 30 min.

$$
\begin{aligned}
60 &= 15(8 - 6) + p(8 - 6 - 1) \\
60 &= 30 + p \\
p &= 30.
\end{aligned}
$$

These examples show the method of using the formula in determining the number of cells required under different conditions of treatment.

COMPARISON OF SIMULTANEOUS AND SEPARATE PUMPING SYSTEMS

The formulas also make it possible to compare the time consumed between discharges when pumping simultaneously with that consumed when pumping separately, other conditions of extraction being the same. If we take, for instance, a series of 6 extractions in 4 cells, $b = 15$ and $p = 5$. With separate pumping n will be $15(8 - 6) + 4(8 - 6 - 5)5 + (12 + 4)5 =$

$$30 - 60 + 80 = 50$$

a will be $30 + (6 + 1)5 = 65$, and

e will be $15 + \dfrac{6 - 2}{2}\, p = 25.$

For a comparison it would not be fair to use b with the same value in simultaneous pumping as in separate pumping because in the latter case, in the example just given, although b is 15, the *actual* total boiling time for each charge, e, is 25 min. $(b + 2p)$; in order to have conditions the same in the two systems. therefore, the value of b in simultaneous pumping (which is always the actual total time of the boiling) must be 25 min. With $c = 4$, $t = 6$, $b = 25$, and $p = 5$ in simultaneous pumping

$$
\begin{aligned}
n &= 25(8 - 6) + 5(8 - 6 - 1) = 50 + 5 = 55 \\
a &= 2b + 2p = 50 + 10 = 60 \\
e &= b = 25.
\end{aligned}
$$

That is, a, the time required between successive discharges of material is a little less in the case of simultaneous pumping.[1] But there is a practical consideration which changes this relation slightly; pumping several cells at the same time is likely to take longer than pumping a single cell, and therefore if p (sim) $= 8$, then a (sim) $= 50 + 16 = 66$ min., and a (sep) $= 30 + 35 = 65$ min., that is, when the pumping time is increased a little to allow for the increased difficulty of pumping several cells instead of one cell, the time required for a complete cycle may be the same or even less in the case of separate pumping.

SUMMARY

1—Formulas have been developed which show the relation between the number of cells and number of treatments in terms of various typical extraction operations both for separate and simultaneous pumping of the solvent in the cells. The formulas for simultaneous pumping are also applicable to continuous extraction processes.

2—These formulas make it possible to determine the number of separate cells or extractors required to furnish a certain number of treatments or extractions for each charge when the time required for each of the various operations is known.

3—With the formulas the time relation between simultaneous pumping and separate pumping has been developed, showing no advantage or very slight advantage for the former.

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[1] Although this is only one case it may be shown that the difference between a (sep) and a (sim), with other conditions the same, is always p when t is even and $\frac{t-1}{t}\,p$ when t is odd.

VAPOR COMPOSITION OF ALCOHOL-WATER MIXTURES

By W. K. Lewis

Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

Received December 18, 1919

In the field of distillation there is no more important problem than the separation of ethyl alcohol from aqueous solutions. Accuracy in the design of apparatus for this separation is absolutely dependent upon exact data as to the composition of the vapors given off by any specific mixture of the two liquids. The data on this point hitherto available in the literature have been inadequate and unreliable. The figures usually accepted are those recalculated for Maercker[1] by Dōnitz from the original experimental results of Grōning. These data check reasonably the results obtained a half century ago by Duclaux.[2] The more recent work of Sorel does not check that of Grōning and is apparently less reliable. The work of Evans[3] is obviously unreliable in view of the fact that he finds the composition of vapor and liquid identical at 92 per cent by weight, whereas a distillate of higher than 95 per cent alcohol can be obtained in commercial practice.

In 1913 Wrewsky[4] published the results of a series of careful determinations of the vapor composition of alcohol-water mixtures, which bear the earmarks of reliability. On the other hand, Wrewsky's work was done, not at constant pressure, but at constant temperature. Furthermore, he operated at only three temperatures, approximately 40°, 55°, and 75° C. His work is, therefore, not directly available for industrial practice because the industrial distillation

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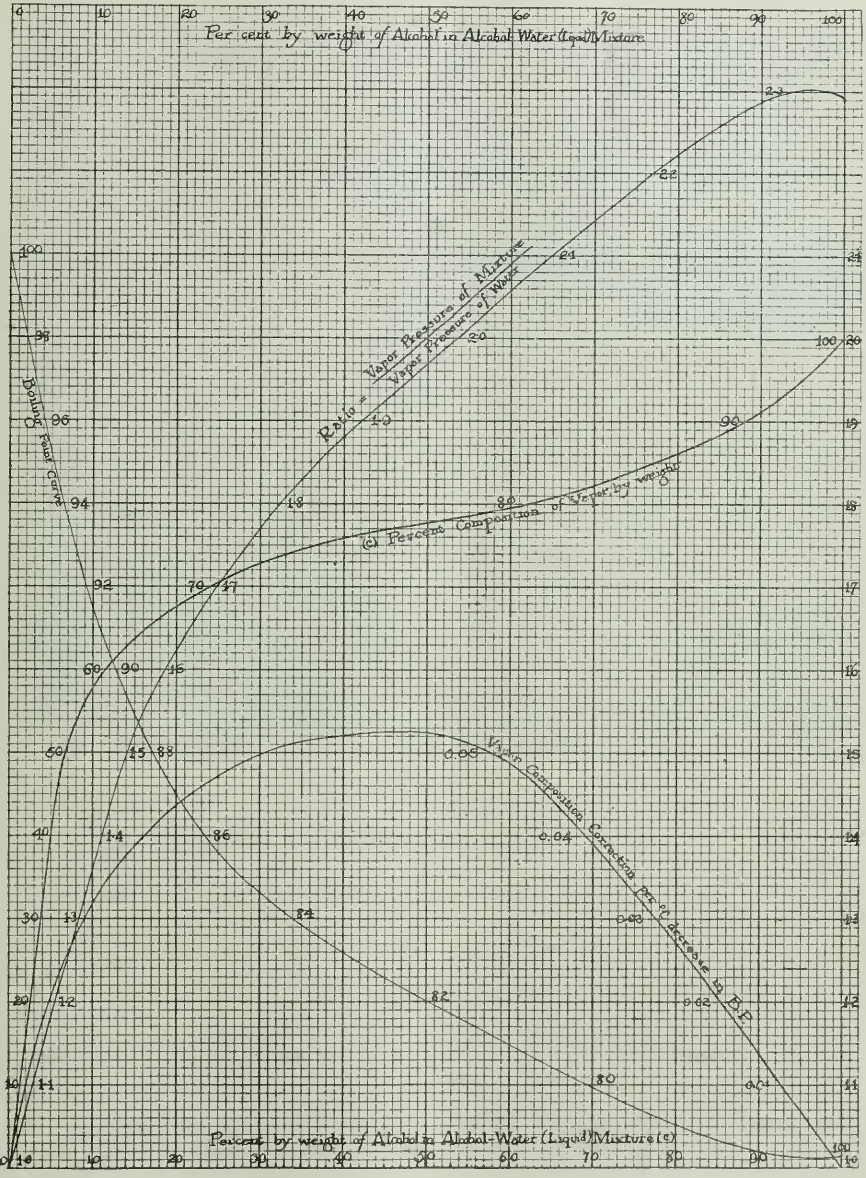
[1] "Handbuch der Spiritus Fabrikation," 7th Ed., Berlin (1898), 590.

[2] *Ann. chim. phys.*, **14** (1878), 305.

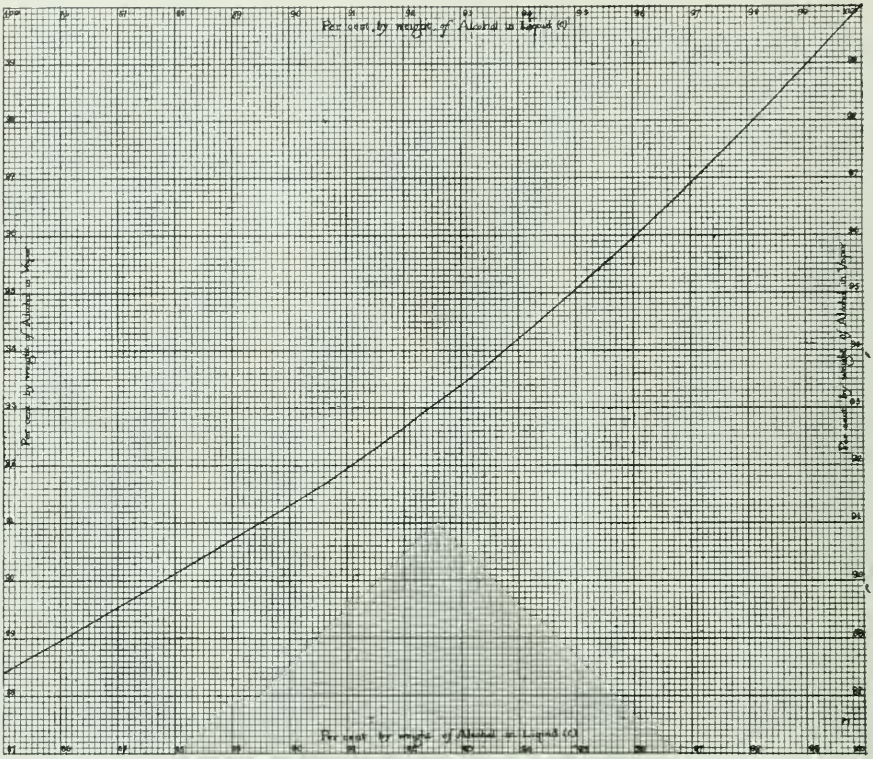
[3] This Journal, **8** (1916), 261.

[4] *Z. phys. Chem.*, **81** (1912), 1.



of alcohol is carried on entirely at temperatures above 78°, *i. e.*, at atmospheric pressure and, in the bottom of rectifying columns, even higher. In order to make these data available for industrial use we have recalculated Wrewsky's results, extrapolating them up to the boiling point. The resulting data are given graphically in the accompanying plots and are believed to be by far the most accurate figures available on the vapor compositions of alcohol-water mixtures.

At each of the temperatures mentioned above Wrewsky determined the vapor composition curve. From these isothermal curves the vapor composition was read off at stated intervals of liquid composition and, for each definite liquid composition, plotted against the temperature. These temperature curves



were extrapolated up to the boiling point of the liquid in question. This gave the vapor composition curve shown in the diagram. Furthermore, the change in vapor composition with change in boiling point was determined from the slope of the temperature curves just described, and plotted to make possible the estimation of vapor composition of liquids boiling at pressures other than atmospheric. The boiling point curve given is from the data of Noyes and Warfle.[1]

The total pressure exerted by any mixture of alcohol and water, at any given temperature, divided by the pressure of pure water at the same temperature, is a ratio which changes but little with change in temperature. The value of this ratio is, of course, unity for water, and rises rapidly with increasing alcohol content of the liquid to approximately 2.3 for alcohol itself. The ratio was determined from the pressure measurements of Wrewsky at the temperatures employed by him, and graphically extrapolated to the boiling point in exactly the same way as the vapor composition. The value of this ratio at the boiling point is plotted as a separate curve, and will make it possible to estimate temperature-pressure relationships other than atmospheric, as for example in the lower part of a rectifying column.

In any problem in alcohol distillation the enrichment is easily realized until the constant boiling mixture is approached. The most important part of the operation and hence of the design is that involved in enrichment above 90 per cent alcohol. It is, therefore, desirable to determine the data above this point with the greatest possible precision and to plot it correspondingly. We have, therefore, appended a separate vapor composition curve for compositions above 85 per cent of alcohol in the liquid.

In order to secure greater accuracy for the vapor composition of these liquids rich in alcohol, the data of Wrewsky within this range were replotted in a somewhat different way. Wrewsky's values for the partial pressures of alcohol and of water, obtained by calculation from the measured values of the total pressure and of the vapor composition, were divided in each case by the pressure of pure alcohol and of pure water at the temperature of the determination. These ratios change but slightly with the temperature. For each of the three temperatures used by Wrewsky they were plotted against the molal composition of the liquid, and smooth curves drawn among the individual points. The ratios were read off these curves for each mol per cent of alcohol in the liquid, and these ratios plotted against the temperature. These last curves, either straight lines or very flat, were extrapolated up to the boiling point, and from the values thus obtained the vapor composition calculated. It will be noted that the extrapolation was in no case greater than four degrees, because the boiling points of these rich alcohol mixtures are nearly constant.

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[1] *J. Am. Chem. Soc.*, **23** (1901), 154

In order to show the applicability of these curves, let it be assumed that a 50 per cent alcohol-water mixture is boiling at a temperature of 100° C. at some point in the lower part of a rectifying column. It is required to determine the composition of the vapor and the pressure under which the liquid is boiling.

Were the liquid boiling at atmospheric pressure it would have a vapor composition at 77.7 per cent. Under these conditions it would boil at 82°. Since it is boiling at 100°, its boiling point has been increased 18° by pressure. From the correction curve it is seen that the vapor composition changes 0.524 per cent per degree. This corresponds to a correction of 0.9 per cent. The correction is positive for a decrease in boiling point and is, therefore, negative for the case in question. Hence the vapor composition of the 50 per cent alcohol at 100° is 76.8 per cent.

At 100° water exerts one atmosphere pressure. It is seen from the vapor pressure ratio curve that a 50 per cent solution exerts 1.97 times as much, *i. e.*, the pressure at the given point in the still is 1.97 atmospheres or 1497 mm.

A SIMPLE METHOD FOR THE PREPARATION OF SODIUM AMALGAM IN FLAKES[1]

By Arthur D. Hirschfelder and Merrill C. Hart
University of Minnesota, Minneapolis, Minn.

Received November 28, 1919

In the course of preparation of saligenin by a slight modification of Hutchinson's method made by Mr. Hurd,[2] it has been necessary for us to use a 2.75 per cent sodium amalgam. This amalgam, when poured on to porcelain plates, forms solid layers, which require a good deal of work and time to reduce to a powder in a mortar. We have been able to prepare a powder of very finely flocculent amalgam by pouring the hot liquid amalgam slowly into a battery jar of xylene or kerosene, which is already being rapidly agitated by an electric stirrer. The amalgam is broken up by the currents as fast as it is poured into the liquid and the fine flocculi settle to the bottom. They are then dried in a current of air on a porcelain plate. When the flocculi are clumped they are readily pulverized by a couple of blows with a pestle.

AN IMPROVED COMPARATOR

By L. H. Cooledge
Michigan Agricultural College, East Lansing, Michigan

Received January 12, 1920

While studying the change in hydrogen ion concentration[3] of water or of a solution of broth due to adding 0.1 cc. of milk to be tested and incubating, the writer found that the time required to match the colors, and to make the necessary changes of tubes to and from the comparator, was so great that a large number of tubes could not be read each hour by the colorimetric method.

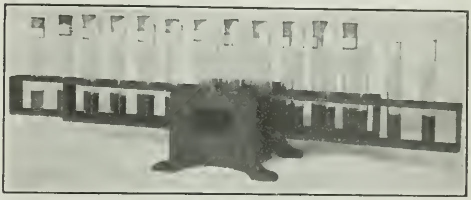

Fig. 1

To make it possible to compare a great number of unknowns with the standard tubes, the comparator of Hurwitz, Meyer and Ostenberg[1] was modified as shown in the accompanying illustrations.

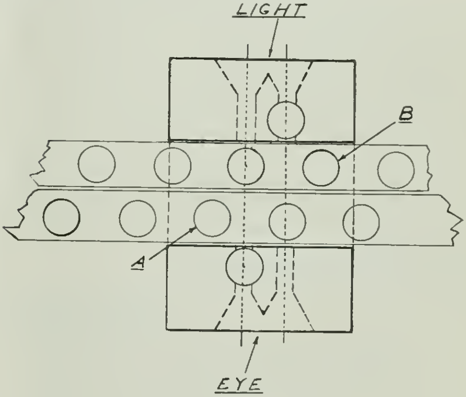

Fig. 2

Two sliding test-tube racks were constructed and so arranged in the comparator that the one carrying the standard tubes, B (Fig. 2), could be slid back and forth until a tube was found that compared in color with the first unknown in the second rack A. The second rack A carrying the unknowns, was then moved along one place and the reading of the second unknown found in the same way. The under surface of each sliding rack was indented opposite each test-tube, the indentation being designed to receive a cog supplied with a spring. By means of this arrangement the tubes stopped with a click at the proper place in the path of light as the racks were moved back and forth. A cog plate and thumb screw to match might be used to facilitate the movement of the sliding racks, but these have not been found necessary. Rack B is so constructed that it can be removed readily and replaced by other racks containing standard tubes for other ranges of P_H.

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[1] From the Department of Pharmacology, University of Minnesota, with the aid of funds granted by the United States Interdepartmental Social Hygiene Board for Research in the prevention and care of venereal diseases.

[2] A. Hutchinson, *Ber.*, **24** (1891), 173; Charles D. Hurd, personal communication.

[3] W. M. Clark and H. A. Lubs, *J. Bact.*, **2** (1917), Nos. 1, 2, and 3.

[1] Johns Hopkins Hospital, *Bulletin* **27** (1916), 16.

The readings may be made by using light directly transmitted or the comparator may be tilted by placing books under the end toward the observer and light may be reflected from a white surface through the tubes.

It is possible by using this improved comparator to examine, in a given time, many times the number of samples which could be examined by the old method.

SUBSTITUTES FOR PLATINUM WIRE IN BEAD AND FLAME TESTS

By C. C. Kiplinger
Mt. Union College, Alliance, Ohio

Received January 2, 1920

One very important source of waste in platinum arises from its extensive use in the qualitative laboratory. The wire alloys with many of the metals with which it comes in contact in the several tests, becomes brittle, breaks, and soon disappears. Under these conditions, the platinum is a total loss.

To avoid this waste it has been found feasible to use a lead pencil "lead" in place of the wire for making bead tests. A piece of the "lead" 5 to 6 cm. in length is held by tongs in the Bunsen flame until the end is red-hot, then dipped in borax and returned to the flame, holding it at such an angle that the borax glass forms a hanging drop on the end of the "lead." This drop constitutes the bead and the tests are made as usual. Each length of "lead" serves for two tests at least, one on each end. Often the graphite can be scraped clean enough to permit of several tests with one piece. If not too large, the bead adheres firmly to the graphite, yet the cold borax glass may be readily removed with a knife. The reducing action of the carbon does not seem to interfere materially.

In a method described by Ehringhaus,[1] a small strip of filter paper is wet with the solution to to be tested and held in the flame, or one end of the paper is placed in the solution and the other end in the flame. The writer has found the latter method very convenient if used in conjunction with the following device: A glass tube 15 cm. long and 6 mm. in internal diameter is bent at an angle of 45° 2 cm. from one end, and the latter is held in the flame until the opening is reduced to a diameter of 3 mm. to 4 mm. A strip of filter paper 4 cm. long is rolled to fit tightly the reduced opening and forced into the tube, leaving about 3 cm. projecting. The longer arm of the tube is filled with the solution to be tested, or with dilute hydrochloric acid, if a powder is to be tested on the paper, and the paper wick is inserted in the flame, holding the tube at such an angle that it feeds properly. A flame of 3 or 4 min. duration can easily be obtained. The burning carbon tends, however, to mask the color of the substances looked for. While this is of no consequence in spectroscopic tests, it is of vital importance in direct vision work. It is possible to eliminate the carbon flame partly by supporting a burner horizontally on a stand, and bringing the upper edge of the paper wick barely within the bottom portion of the flame. The salt solution is vaporized and colors the flame with a minimum consumption of paper.

A clean iron nail not less than 3 mm. in diameter will be found to be of value in these tests. Owing to the relatively large surface offered by the head of the nail, the latter seems peculiarly adapted for this purpose. The nail can be easily cleaned and burned free from sodium, and in general the spectra of the iron salts do not interfere.

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[1] *Chem. Abs.*, **13** (1919), 3115.

SCIENTIFIC SOCIETIES

FIFTY-NINTH MEETING AMERICAN CHEMICAL SOCIETY, ST. LOUIS, MO., APRIL 12 TO 16, 1920

PROGRAM OF PAPERS

GENERAL SESSION

Henry W. Kiel, Mayor of St. Louis. **Address of Welcome.**

W. A. Noyes, President, American Chemical Society. **Response.**

Paul W. Brown, Editor, *America at Work*. **The Physical Basis for the Economic Development of the Mississippi Valley.**

Chas. H. Herty, Editor, *Journal of Industrial and Engineering Chemistry*. **Victory and Its Responsibilities.**

Amos A. Fries, Director, Chemical Warfare Service. **Chemical Warfare.**

J. H. Hildebrand. **The Prediction of Solubility.**

Victor Lenher. **Selenium Oxychloride, a Neglected Inorganic Solvent.**

E. T. Wherry. **Studying Plant Distribution with Hydrogen Ion Indicators.**

G. H. A. Clowes. **Adsorption of Alkaloids.**

O. H. Pierce. **The Chemical Resources of the St. Louis District.**

AGRICULTURAL AND FOOD CHEMISTRY DIVISION

C. E. Coates, *Chairman* T. J. Bryan, *Secretory*

1. C. E. Coates. **Louisiana Molasses and Sirup.**
2. George Defren. **The Use of Refined Edible Lactic Acid in Food Products.**
3. H. S. Grindley. **Preliminary Feeding Experiments with Pigs to Determine the Nutritive Value of the Amino Acids of the Proteins of Feedingstuffs. (Lantern.)**
4 C. T. Dowell. **Proteins of Pecans.**
5. Fred H. Smith. **Body Fat of Hogs Fed on Peanuts.**
6. J. W. Reed. **An Accurate and Rapid Dry Combustion Method for the Simultaneous Determination of Soil Organic Matter and Organic Carbon.**
7. J. W. Reed and R. H. Ridgell. **The Actual Carbon Content of Soil Organic Matter and Its Relation to the Use of Conventional Factor.**
8. W. D. Richardson. **Limitations of the White Rat as an Experimental Animal.**
9. W. D. Richardson. **Mammalian *vs* Avian Dietary Experiments.**
10. Herbert Bailey and W. D. Baldsiefen. **The Ether Insoluble Hexabromides of Pure and Adulterated Linseed Oils.**
11. J. S. Hughes and E. F Ferrin. **The Relative Nutritive Value of Alfalfa as a Supplement to a Diet of Corn and Tankage and Kaffir and Tankage.**
12. Jay Barton. **Data on Bacterial Count of Beverages in Missouri.**
13. C. O. Swanson. **Hydrocyanic Acid Present in Sudan Grass.**
14. C. O. Swanson and W. L. Latshaw. **Effect of Alfalfa on the Sulfur of the Soil in Comparison with Grain Crops.**
15. L H. Almy and E Field. **The Preservation of Fish Frozen in Chilled Brine. I—The Penetration of Salt.**

BIOLOGICAL CHEMISTRY DIVISION

R A. Gortner, *Chairman* A. W. Dox. *Secretory*

1. C. O. Johns and H. C. Waterman. **Some Proteins from the Georgia Velvet Bean, *Stizolobium Deeringianum*. (Lantern.)**
2. C. O. Johns and A. J. Finks. **The Deficiency of Cystine in Proteins of the Genus *Phaseolus*. (Lantern.)**
3. P. A. Kober. **Studies on Neoarsphenamines.**
4. R. A. Gortner and George E. Holm. **On the Colorimetric Estimation of Tyrosin by Folin's Phenol Reagent.**
5. George E. Holm and R A. Gortner. **On the Origin of the Humin Formed by the Acid Hydrolysis of Protein. VI—The Effect of Acid Hydrolysis upon Tryptophane.**
6. M. X. Sullivan and R. E. Stanton. **The Alkali Reserve in Pellagra.**
7. S. L. Jodidi, S. C Moulton and K. S. Markley. **The Mosaic Disease of Spinach as Characterized by its Nitrogen Constituents.**

8 B. M Duggar. The Effect of Conditions on the Relation of Seed Plants to H-Ion Concentration of Nutrient Solutions.
9. W. H. Chambers. The Relation of Dextrose to H-Ion Concentration with *Bacillus Coli.*
10. Richard D. Bell and Edward A. Doisy. The Determination of Small Amounts of Chlorine in Tissues.
11. H. E. Patten and T. O. Kellems. Pectin Studies. I—Effect of Pectin on the Hydrogen Ion Concentration of Acid and of Alkaline Solutions.
12. P. A. Schaffer. The Oxidation of Acetoacetic Acid by Hydrogen Peroxide in the Presence of Glucose.
13. A. W Dox and Lester Yoder. Influence of Fermentation on the Starch Content of Experimental Silage.
14. A. D. Emmett and Mabel Stockholm. Water-Soluble β-Vitamines: Are the Antineuritic and the Growth-Promoting Vitamines the Same?
15 A. D. Emmett and Marguerite Sturtevant. The Fat-Soluble A. Vitamine and Xerophthalmia.
16. C. R. Moulton. Biological Changes in the Flesh of Beef Animals during Partial Starvation.
17. J. S. Hughes and F. E. Fox. Scurvy in Poultry.
18 J. S. Hughes and J. B Fitch. The Relation of the Vitamine Content of Feed to the Vitamine Content of Milk Produced.
19. Victor E. Levine and Eben J. Carey. Studies in Embryo-Chemistry. I—The Enzymes of the Embryonic Pancreas. A. Lipase.
20. Victor E. Levine. A New Test for Sugar in the Urine.
21. Edgar J. Witzemann. Disodium Phosphate as a Specific Catalyst for the Quantitative Oxidation of Glucose to Carbon Dioxide with 3 Per cent H_2O_2.
22. Harper F. Zoller. The Standardization of the Borax Solubility Test for Commercial Casein and Its Application. (Lantern.)
23. Harper F. Zoller. The Precipitation of Grain Curd Casein from Pasteurized Milk Including Pasteurized Sweet Cream Buttermilk. (Lantern.)
24. Mansfield Clark, Harper F. Zoller A. O. Dahlberg and A. C. Weimer. Grain Curd Casein. (Lantern.)
25. Harrison Hale. Chlorine as a "Flu" Preventive.
26. Howard B. Lewis and Lucie E. Root. The Synthesis of Lysine in the Organism of the White Rat.
27 C. H. Bailey and A. M. Gurjar. Respiration in Cereals. II—The Respiration of Sprouted Wheat. (By title.)
28. C. H. Bailey and A. M. Gurjar. Respiration in Cereals. III—The Respiration of Rice Paddy and Milled Rice. (By title.)
29. C. H. Bailey and A. M. Gurjar. Respiration in Cereals. IV—The Respiration of Frosted Wheat Plants. (By title.)
30. C. H Bailey and A. M. Gurjar. Respiration in Cereals. V—The Respiration of Wheat Plants Infected with Stem Rust. (By title.)
31. S. D. Wilkins and R. A. Dutcher. The Etiology of Limberneck in Fowls. (By title.)
32. S. D. Wilkins and R. A. Dutcher. The Relation of Vitamines to the Development of Sex Organs in Cockerels. (By title.)
33. V. E. Nelson and A. R. Lamb. The Effect of Vitamine Deficiency on Various Species of Animals. I—The Production of Xerophthalmia in the Rabbit. (By title.)
34. E. I. Fulmer, F. S. Sherwood and V. E. Nelson. The Role of Vitamines in the Growth of Yeast. Are Vitamines Essential? (By title.)
35. W. P. Bovie. A Correction of Two Previous Papers: (1) Rate of Recovery from the Action of Fluorite Rays. (2) Sensitization to Heat Due to Exposure to Light of Short Wave Lengths.
36. W. P. Bovie. The Graphical Representation of Hydrogen Ion Concentration.
37. W. P. Bovie. Some Notes Concerning Formol Titration of Nitrogen.

DYE SECTION

Charles L. Reese, *Chairman* R Norris Shreve, *Secretary*

1. S. A. Tucker. Dye Patents of the Chemical Foundation, Inc.
2. W. F. Meggers and F. J. Stimson. Dyes for Photographic Sensitizing. (Lantern.)
3. J. F. Ragsdale. Anthranilic Acid, Purity and Tests of the Commercial Product.
4. L. A. Watt. Ortho-chlor-para-toluol Sulfonate, Purity and Tests of the Commercial Product.
5. Launcelot W. Andrews. Uses of Formic and Oxalic Acids in the Dyeing Industry.
6. George Heyl. Synthetic Dyes as Applied to Chemicotherapy and Microscopy.
7. Robert E. Rose. Dye Research.
8. I. M. Bernstein. The Hydrogen Exponent in the Classification of Indicators and Some of Its Applications.
9. F. L. English. Application of $TiCl_3$ in Analysis of Intermediates.
10. C. L. Knowles. Some Physical Constants of Pure Aniline. (By abstract.)
11. E. Q. Adams. The Absorption Spectra of the Nitric Esters of Glycerol. (Lantern.)
12. L. A. Mikeska. Tetramethylquinolines. (Lantern.)
13. J. A. Ambler. Naphthalene Sulfonic Acids. Some Difficultly Soluble Salts of Naphthalene Sulfonic Acids. (Lantern.)
14. J. A. Ambler. A Method for the Qualitative Detection of Some Naphthalene Sulfonic Acids. (Lantern.)
15. C. E. Senseman. The Preparation of Disulfonic Acids from Benzene Monosulfonic Acid. (Lantern.)
16. H. L. Haller. Synthesis of *sym*-Xylidine. (Lantern.)
17. Max Phillips and H. D. Gibbs. Alkali Fusions. II—The Fusion of Sodium Benzene Disulfonate with Sodium Hydroxide for the Production of Resorcinol.
18. Max Phillips and H. D. Gibbs. A Synthesis of Thymol from *p*-Cymene. (Lantern.)
19. K. P. Monroe. The Vapor Pressure of Phthalic Anhydride. (Lantern.)
20. K. P. Monroe. A New Source of Furfural and an Investigation of the Preparation and Properties of "Furfural Green." (Lantern.)
21. Robert E. Hussey. The Present Independence of American Synthetic Dyes and How It Was Accomplished.

INDUSTRIAL AND ENGINEERING CHEMISTRY DIVISION

H. D. Batchelor, *Chairman* H. E. Howe, *Secretary*

I—Symposium on Cellulose Chemistry

1. Jessie E. Minor. The Mechanism of the Reactions of Cellulose.
2. S. A. Mahood. Some Observations on the Determination of Cellulose in Wood.
3. R. C. Woodbridge, Jr. Nitrocellulose from Wood Pulp.
4. J. O. Small and C. A. Higgins. Notes on the Manufacture of Nitrocellulose.
5. G. J. Esselen Certain Aspects of the Chemistry of Cellulose Acetate from the Colloidal Viewpoint.
6. H. E. Howe. Projects of the Preliminary Committee on American Cotton Research.
7. Jasper E. Crane. Is It Advisable to Form a Section of Cellulose Chemistry?
8. L. F. Hawley. Some Observations on the Determination of Cellulose in Wood.
9. H A. Levey Cellulose Phthalate: Its Preparation and Properties.

II—Papers

1. Clarence W. Balke. Effect of Impurities on the Metallurgy of Tungsten.
2. W. D. Turner and K. K. Kershner. Separation and Examination of the Isomers of Xylene.
3. H. L. Dunlap and K. K. Fischlowitz. Preparation of Furfural from Corn Cobs.
4. H. L. Dunlap and K. K. Kershner. Carbonization of Missouri Cannel Coals.
5. W. D. Collins. Problems in Specifications for Reagent Chemicals.
6. Thos. B. Freas. The Standardization of Laboratory Apparatus and Instruments in Respect to Quality, Shape, Size, and Packing.
7. I. N. Kugelmass. Recovery of the Grease from the Soapy Wash Waters in Laundering.
8. I. N. Kugelmass. A Rapid Soap Dissolving-Distributing System.
9. Merle Randall. The Recovery of Iodine from Kelp.
10. Victor Lenher. Selenium and Tellurium.
11. W. J. Hale. A Plan for Incentive to Research in Pure and Applied Chemistry.
12. A. M. Comey. The Economic Status of the Chemist. (Lantern.)
13. Edward J. Mahin. Crystal Growth in Bearing Metals. (Lantern.)
14. F. W. Bushong. The Specific Heat of Petroleum at Different Temperatures. (Lantern.)
15. D. R. Sperry. The Application of the Filter Press to Problems in Chemical Industry.
16. D. T. Shaw. Chemical Corrosion.
17. W. D. Richardson. The Solution of Metal in Acids as Related to Corrosion.
18. W. D. Richardson. A Suggested Basis for an Index of Corrosion for Iron and Steel.
19. W. D. Richardson. A New Type of Catalyzer for the Hydrogenation of Oils and Other Purposes.
20. F. C. Vilbrandt, S. L. Shenefield and James R. Withrow. Sulfites as Standards for Oxidizing Reagents.
21. D. C. Mapes. The Crystalline Structure of Paraffin Wax.
22. C. K. Francis. Mid-Continent Gasoline.
23. J. Culver Hartzell. The Relation of Chemistry (Analytical and Thermal) to the Fabrication of Steel.
24. J. Culver Hartzell. The Relation of the Electric Furnace to the Fabrication of Carbon and Alloy Steels, with Special Reference to the Chemical and Physical Changes Produced.
25. O. L. Barnebey. Industrial Uses of Activated Charcoal.
26. Edward J. Mahin. Inclusions and Ferrite Crystallization in Steel: II—Solubility of Inclusions.
27. Herbert Bailey and C. B. Edwards. The Determination of the Specific Heat of Heavy Mineral Oils.
28. W. C. Holmes. The Freezing Points of Mixtures of Sulfuric and Nitric Acids. (By title.)

29. W. C. Cope. Strength and Velocity of Detonation of Various Military Explosives. (By title.)
30. J. W. Turrentine. Potash and Reconstruction. (By title.)
31. J. W. Turrentine. The Experimental Kelp-Potash Plant of the U. S. Department of Agriculture. 2nd Report. (By title.)
32. Alfred R. Powell. A Study of the Reactions of Coal Sulfur in the Coking Process. (By title.)
33. Alfred R. Powell. The Desulfurizing Action of Hydrogen on Coke. (By title.)
34. Alfred R. Powell. The Analysis of Sulfur Forms in Coal. (By title.)

LEATHER CHEMISTRY SECTION

Louis E. Levi, *Chairman* William Klaber, *Secretary*

1. John Arthur Wilson and Erwin J. Kern. The True Tanning Value of Vegetable Tanning Materials.
2. John Arthur Wilson and Edwin A. Gallun. The Neutral Salt Effect and Its Bearing upon Leather Manufacture.
3. Erwin J. Kern. The Determination of Sulfate in Sulfonated Oils.
4. Arthur W. Thomas. A New Method for the Determination of Sulfuric Acid in Leather.
5. Arthur W. Thomas and M. J. Kelly. Time Factor in the Adsorption of the Constituents of Chromi-Sulfate Solutions by Hide Substance.
6. Arthur W Thomas and S. B. Foster. The Conductivity Titration of Chrome Liquors.
7. I. Newton Kugelmass. Physico-Colloidal Interpretations of the Tanning and Tawing Procedures.
8. Edward E. Marbaker. The Currying of Leather for Belting.
9. Louis E. Levi. Chemical Work in the Tannery.

ORGANIC CHEMISTRY DIVISION

E. Emmet Reid, *Chairman* Roger Adams, *Secretary*

1. W. D. Turner and A. M. Howald. Methylamines from Carbinol and Ammonium Chloride.
2. K. K. Kerschner and W. D. Turner. The Synthesis and Physical Constants of Benzene and Toluene Sulfonamides.
3. T. C. Whitner, Jr., and E. Emmet Reid A Sulfide Alcohol.
4. Y. Uyeda and E. Emmet Reid. A Sulfide Acid.
5. R. E. Rindfusz and V. L. Harneck. Heterocyclic Compounds from N-Arylamino Alcohols.
6. I. N. Hultman, Anne W. Davis and H T Clarke. Use of the Automatic Separator in Organic Preparations.
7. W. L. Lewis and W. V Evans. Condensed Rings Containing Arsenic.
8. Roger Adams, O. Kamm, H. T. Clarke and J. B. Conant. A Co-operative Pamphlet on Organic Chemical Preparations.
9. Roger Adams and J. B. Segur. The Preparation and Physiological Action of Oxazolidones and Their Decomposition into Substituted β-Amino Ethyl Alcohols.
10. Roger Adams, H. E. French and L. H. Ulich. The Reaction between Aldehydes and Acid Halides.
11. Oliver Kamm and C. S. Palmer. The Kaufler-Cain Formula for Diphenyl Derivatives.
12. Oliver Kamm and J. H. Waldo. β,β'-Dichlorodiethyl Ether: The Oxygen Analog of Mustard Gas.
13. A. W. Homberger and M. Borries. Chlorination of Acetone.
14. C. W. Cuno. The Use of a Chart in Studying Organic Chemistry.
15. Henry Gilman. The Mechanism of Some Reactions Involving the Grignard Reagent.
16. L. C. Raiford. The Nitration of Certain Halogenated Phenols.
17. Ralph C Huston. The Action of Aromatic Alcohols on Phenols in the Presence of Aluminum Chloride.
18. Arnold E. Osterberg and E. C. Kendall. Derivatives of Cyclohexane.
19. H. C. P. Weber. The Formulation of Organic Reactions under the Electron Conception of Valence. Reaction of Formaldehyde.
20. Victor E. Levine. A New Color Reaction for Phenols Based upon the Use of Selenious Acid.
21. Victor E. Levine. A Note on the Differentiation of Acetic Anhydride from Glacial Acetic Acid.
22. Hilton Ira Jones. The Poly-phenyl Ethers.
23. Harper F. Zoller. Oxalyl Chloride in the Synthesis of Triphenylmethane Dyes.
24. Fred W. Upson. The Decomposition of Amines at High Temperatures.
25. T B Aldrich. The Benzoic Acid Ester of Trichlortertiary Butyl Alcohol.
26. Treat B. Johnson and P. G. Daschavsky. The Utilization of Waste in Silk Fibroin. (By title.)
27. Treat B. Johnson, Arthur J. Hill and Erwin B. Kelsey. The Conversion of Anilides of Chloroacetic Acid into Ketide-Isothiocyanates. (By title.)
28. Treat B. Johnson and J. B. Fishman. The Condensation of Formaldehyde with *o*-Nitrophenol. (By title.)
29. Arthur J. Hill and J. J. Donleavy. The Alkylation of Aromatic Amines by Heating with Alcohols. (By title.)
30. Treat B. Johnson and L. A. Mikeska. The Search for Pressor Substances in the Pyrimidine Series. (By title.)
31. Wm. L. Evans and Lily Bell Sefton. The Oxidation of Isopropyl Alcohol by Means of Alkaline Potassium Permanganate.

PHARMACEUTICAL CHEMISTRY DIVISION

Charles E. Caspari, *Chairman* Edgar B. Carter, *Secretary*

1. Jules Bebie. Stability of Chloramine Antiseptics.
2. Carl Nielsen. Chemistry and Pharmacology of the Chloramines.
3. Wilbur L. Scoville. Colorimetric Estimation of Adrenalin.
4. H. V. Farr. Improved Methods for Arsenic Estimation.
5. L. A. Watt. The Melting Point and the Determination of Free Salicylic Acid in Acetyl Salicylic Acid.
6. Herbert C. Hamilton. Biological Methods for Digitalis Assay.
7. E. H. Vollweiler. Researches on Hypnotics.
8. Roger Adams. Researches on Anesthetics.
9. Chas. Baskerville. Wood Alcohol and Prohibition.
10. G. H. A. Clowes and A L. Walters. Drug Absorption in the Intestinal Tract.

PHYSICAL AND INORGANIC CHEMISTRY DIVISION

Wm. D. Harkins, *Chairman* H. N. Holmes, *Secretary*

I—Colloid Symposium

1. Jerome Alexander. Some Practical Applications of Colloid Chemistry.
2. Wilder D. Bancroft. Gelatinous Precipitates.
3. Martin H. Fischer. The Colloid Chemistry of Soaps.
4. John Arthur Wilson. Vegetable Tanning as a Colloid Chemical Process.
5. A. V. Bleininger. Ceramics from the Colloid Viewpoint.
6. W. D. Harkins. Surface Energy.
7. Arthur W. Thomas. Nomenclature in Colloid Chemistry. A Plea for Reform.

II—Papers

1. Gerald L. Wendt and A. C. Grubb. A New Form of Active Nitrogen.
2. Gerald L. Wendt, Robert S Landauer and A. C. Grubb. The Ozone Form of Hydrogen at Atmospheric Pressure. The Formation of Ammonia.
3. S. C. Lind and L. D. Roberts. New Determination of the Absolute Value of the Radium:Uranium Ratio.
4. S. Dushman and Irving Langmuir. A General Theory of Chemical Reactivity, Calculations of Reaction Velocities, Equilibrium Constants, and Vapor Pressures.
5. W. A. Noyes and George H Coleman. The Direct Combination of Nitrogen and Chlorine.
6. Wilbert J. Huff. The Causes and Prevention of After-Corrosion on the Bores of Firearms.
7. J. B. Ferguson and A. F. Buddington. The Binary System, Akermanite-Gehlenite. (Lime, Magnesia, Alumina, Silica.)
8. E. W. Posnjak and H. E. Merwin. The System Fe_2O_3–SO_3–H_2O.
9. James Kendall. The Ionization of Strong Electrolytes.
10. J. H. Mathews. Heats of Vaporization. (Lantern.)
11. R. O. E Davis, L. B. Olmstead and F. O. Lundstrum. The Vapor Pressure of the Ammonia-Lithium Nitrate System. (Lantern.)
12. R. O. E. Davis, L. B. Olmstead and F. O. Lundstrum. The Vapor Pressure of the Ammonia-Calcium Nitrate System. (Lantern.)
13. R. B. Sosman and H. S. Roberts. Magnetic Properties of Dilute Solutions of Certain Metallic Oxides in Silicate Glasses. (Lantern.)
14. Farrington Daniels and Arthur C. Bright. Pressure Measurements of Corrosive Gases: The Vapor Pressure of Nitrogen Pentoxide. (Lantern.)
15. F. O. Anderegg. The Formation of Ozone and Nitric Acid from Air in the High Frequency Corona. (Lantern.)
16. W. S. Hendrixson. Electrometric Titration of Iodides and a Practical Potentiometer for Such Work. (Lantern)
17. William D. Harkins. The Existence of the Nucleus of the Meta-Hydrogen, the Possible Presence of Meta-Hydrogen in Hydrogen, and the Evidence Which Indicates that the Elements Magnesium, Silicon, Nickel, Copper, Zinc, and Other Elements of the Atomic Numbers from 28 to 80 (Mercury) Are Mixtures. The Function of Binding and Cementing Electrons. (Lantern.)
18. James C. McCullough. A Method of Welding Thermocouples in the Electric Arc.
19. Hamilton P. Cady, Howard McKee Elsey and Emily V. Berger. The Solubilities of Helium.
20. I. N. Kugelmass. Washing in Hard Water in the Presence of Colloidal Organic Hydrosols.
21. Harry N. Holmes. Mineral Oil-Soap Jellies as a Foundation for Greases.
22. S. E. Sheppard and Felix A. Elliott. A Photometric Method for the Study of Colloids and Some Applications to Gelatine.
23. G. H. A. Clowes. Protoplasm and Fuller's Earth.
24. Arthur Mutscheller. On Colloidal Adsorption: The Heterogeneous Equilibrium between Colloids and Ions.
25. Felix A. Elliott and S. F. Acree. A New Form of Hydrogen Electrode Apparatus.

26. Felix A. Elliott and S. F. Acree. Preliminary Note on the Use of the Hydrogen Electrode for Measuring the Separate Ionization Constants of Polyacids and Bases; Specifically Tartaric Acid.
27. Felix A. Elliott and S. F. Acree. The Use of the Hydrogen Electrode in Measuring the Ionization of Acid Salts.
28. Alan W. C. Menzies. A Surface Condensation Error in Certain Measurements of Vapor Pressure by the Gas Current Saturation Method.
29. Alan W. C. Menzies. The Explanation of the Tamman-Schottky-Partington Anomaly.
30. Alan W. C. Menzies. A Differential Thermometer.
31. Albert F. O. Germann. The Crystallization of Glass: A Surface Phenomenon. The Repair of Crystallized Glass Apparatus.
32. William D. Harkins and C. E. Broeker. The Separation of the Element Chlorine into Chlorine and Meta-Chlorine.
33. William D. Harkins and Lester Aronberg. A Force, Apparently Due to Mass, Acting on an Electron, and the Non-Identity of Isotopes in Spectra and Other Properties.
34. Eric K. Rideal. Radiation and Chemical Reactivity.
35. Albert G. Loomis. A Study of the System Ammonia–Magnesium–Mercury.
36. Ralph E. Hall. The Influence of Pressure on the Electrolytic Conduction of Aqueous Solutions.
37. C. J. Rottmann. A New Form of Portable Standard Cell.
38. Harry B. Weiser. Hydrous Oxides. II—Hydrous Aluminum Oxide.
39. Harry B. Weiser. Factors Determining the Degree of Reversibility of Precipitation of Colloidal Hydrous Oxides.
40. Harry B. Weiser and Everett E. Porter. Spontaneous Evaporation.
41. William D. Harkins and Y. C. Cheng. Negative Surface Energy.
42. William D. Harkins and A. Morton. The Formation of Ammonia from Nitrogen and Hydrogen in the Corona.
43. Merle Randall and C. C. Scalione. The Electrical Conductivity of Dilute Aqueous Solutions of the Alkali Hydroxides.
44. Merle Randall. The Partial Molal Volume of the Constituents in Solutions of Electrolytes.
45. H. H. Willard and R. K. McAlpine. A Revision of the Atomic Weight of Antimony. Preliminary Report.
46. H. H. Willard and Dorothy Hall. A Separation and Volumetric Determination of Cobalt.
47. H. H. Willard. A New Form of Filtering Crucible.
48. L. J. Desha. Quantitative Measurement of Fluorescence.
49. Wm. H. Blanchard. Notes on the Determination of Chromium as Chromic Oxide.
50. Victor E. Levine. The Preparation of Colloidal Selenium.
51. Chas. W. Cuno. A Theory of Catalytic Action.
52. W. M. Sternberg. Some Applications of Sodium Peroxide in Analytical Chemistry.
53. J. H. Hildebrand, P. S. Danner and B. M. Burchfield. The Conductivity of Ethyl Alcohol.
54. H. S. Fry. Electronic Formulas of Metal-Ammines. (By title.)
55. George W. Sears. The Separation and Detection of Arsenate and Arsenite. (By title.)

RUBBER DIVISION

W. K. Lewis, *Chairman* Arnold H. Smith, *Secretary*

1. Discussion of Report of Committee on "Physical Testing."
2. W. K. Lewis and Wm. H. McAdams. Bromine Addition to Rubber.
3. J. M. Bierer. Relative Value of Shoddy in Mechanical Rubber Goods.
4. W. K. Lewis. Recovery of Volatile Solvents in the Rubber Industry.
5. W. J. Kelly. The Determination of True Free and True Combined Sulfur in Vulcanized Rubber.
6. S. W. Epstein. Analytical Determination of the Coefficient of Vulcanization.
7. G. D. Kratz and A. H Flower. Small Amounts of Magnesia and Certain Organic Substances as Accelerators.
8. W. K. Lewis and F. P. Barker. Dispersing Power of Pigments.
9. C. O. North. The Effect of Compounding Ingredients on the Physical Properties of Rubber. (Lantern.)
10. H. J. Masson and Irene Diner. Microscopic Examination of Rubber Products. (By title.)
11. E. B. Spear. Rubber Chemistry from the Colloidal Viewpoint.
12. Symposium on the Testing of Pigments. Led by W. W. Evans.

SUGAR SECTION

C. A. Browne, *Chairman* Fred. J. Bates, *Secretary*

1. S. J. Osborn. Chemical Control in the Beet Sugar Industry.
2. C. A. Browne. The Testing of Saccharimeters by Means of the Telescopic Control Tube.
3. C. A. Browne. Observations upon the Use of Different Types of Saccharimeters.
4. Walter L. Jordan. The Filtration of Sugar Juices and Sirups.
5. F. W. Zerban. The Clarification of Cane Juice with Diatomaceous Earth and Decolorizing Carbon.
6. G. P. Meade and J. B. Harris. The Hess-Ives Tint Photometer and Its Use with Raw Sugars.
7. N. Kopeloff and H. Z. E. Perkins. Deterioration of Cuban Raw Sugar in Storage.
8. Noel Deerr. The Development of the Polarimeter.
9. A. F. Blake. Changes in the Analytical Ratios of Sugar during Refining.
10. W. D. Horne. Boneblack and Decolorizing Carbons.
11. N. Kopeloff and Lillian Kopeloff. The Production of the Gum, Levan, by Mold Spores.
12. V. L. Aiken. The Determination of Moisture in Beet Sugar Factory Products.

WATER, SEWAGE AND SANITATION DIVISION

J. W. Ellms, *Chairman* W. W. Skinner, *Secretary*

1. Edward Bartow. Sewage Disposal Committee of the National Research Council.
2. R. E. Greenfield and G. C. Baker. Relation of H-Ion Concentration and Carbon Dioxide in Natural Waters.
3. G. C. Baker. Preparation of Ammonia-Free Water.
4. W. W. Skinner and J. W. Sale. Sewage Treatment at Fort Myer.
5. M. Starr Nichols. The Nitrate Content of 500 Waters Which Were Considered Potable from a Bacteriological Standpoint. (Lantern.)
6. Harry E. Jordan. Seasonal Variations of Bacterial Flora during Filtration Process.
7. W. W. Skinner and J. W. Sale. A Study of Sewage and Trade Wastes at Bridgeport, Conn.

AMERICAN ELECTROCHEMICAL SOCIETY

The Spring Meeting, held at Boston, April 8 to 10, 1920, was one of the best meetings of recent years. A well-prepared program of nearly fifty papers was the main attraction, supplemented by visits to plants and social features of unusual drawing power. As a result, over two hundred and fifty members of the Society signed the register, and all the features of the meeting were well attended.

Over forty of the papers were available as preprints, thus adding materially to their intelligent discussion, and rendering unnecessary the tedious reading of papers *in extenso* by a laboring author to a usually bored audience.

The sessions of Friday, April 9, were held jointly with the American Institute of Electrical Engineers.

The Thursday session, held in Huntington Hall, Rogers Building, one of the old "Technology" buildings, opened with the annual business meeting of the Society. Professor Talbot welcomed the visitors on behalf of the Institute. The treasurer's report showed that income just about balanced expenditures in 1919, even when including under the latter item $2,000 invested in Victory Loan bonds. With annual dues still at five dollars, the Society is certainly establishing for itself an enviable record for economical management in these days of strenuous financing to meet the acid test of H. C. L. The secretary's report showed an increase of membership in 1919 of 306, due largely to the successful activity of Mr. Schluederberg, chairman of the membership committee. The present membership is over 2400.

The tellers of election reported on the voting for new officers as follows:

President: W. S. Landis, Chief Technologist of the American Cyanamid Company.

Vice Presidents: J. A. Mathews, President of the Holcomb Steel Company, L. E. Saunders, Manager of Abrasive Plants of the Norton Company, A. T. Hinckley, Chemist of the National Carbon Company.

Managers: Colin G. Fink, Research Director of the Chile Exploration Company, Acheson Smith, President of the Acheson Graphite Company, H. B. Coho, Business Engineer of the National Lead Company.

Treasurer: P. G. Salom, of Philadelphia.

Secretary: J. W. Richards, Professor of Metallurgy at Lehigh University.

The question of the Society's approving the establishment of the metric system as the only legal standard of weights and measures in the United States was brought up and by motion referred to a referendum of the Society, as a guide to the Board of Directors in taking action for the Society. President Bancroft announced the death, in February, of Prof. H. S. Carhart, who was the second president of the Society in 1904–5.

The scientific business of the meeting began with an address by the retiring president, Prof. Bancroft, on "Contact Catalysis," which reviewed thoroughly the history and present status of this knotty problem. It will be found intensely interesting by everyone seeking light on these little understood phenomena. This was followed by a "Symposium on Colloid Chemistry," which contained some notable contributions. Hulett and Nelson, in a long and brilliant paper, brought forward experimental proof that so-called graphitic acid is a colloidal oxide of carbon. They assign it the formula C_4O or $C_{11}O_3$, and describe its properties. Selvig and Ratliff, of the Bureau of Mines (Pittsburgh), discussed the analytical determination of graphitic carbon in various materials. W. C. Moore described examples of selective adsorption by the bacteria *B. pyocyaneus*—an essentially colloidal action. W. A. Deane, of the Dorr Concentrator Company, discussed at length "settling" problems, showing how they involved the detailed utilization and application of all the information we possess about the principles of colloid chemistry; in fact, the practical observations of Mr. Deane go far to explain some so-far unexplained colloid phenomena, such as the stratification of settling solutions. Mr. Deane has made a splendid contribution to applied colloidal chemistry. The other papers presented at this session were: Goodwin and Knobel, on the effect which alternating current, superposed on direct current, has on the over-voltage of hydrogen; Holler and Ritchie, on the concentration of hydrogen ions in dry cells, and its effect on the voltage of the cells; MacInnes, Adler and Joubert on the exact chemical reactions taking place in the lead accumulator, in which they proved that no higher oxide than PbO_2 is formed; Wm. R. Mott, on flame colorations and condensed coatings obtained by introducing substances into the arc. The last paper dealt with several new methods of detection of elements, particularly the rarer ones, and is highly commended as rich in new analytical data of wide practical application.

After lunch, taken in the Walker Memorial Building at the new Institute of Technology group in Cambridge, the afternoon session was held in one of the numerous fine lecture rooms, the particular one selected happening to have "Faraday" inscribed over its portal. With an assembly which taxed the capacity of the hall, many students of "Tech" and Harvard being present, the following papers were read and discussed: W. S. Landis, on the new cyanide formed by fusion of calcium cyanamide with salt and some calcium carbide, in a quick-melting electric furnace, forming a mixture of calcium chloride and sodium cyanide (25 to 40 per cent of the latter), which is sold and used for its cyanide content only; C. J. Rottman, on exact and quick determination of carbon in ferro-alloys—a difficult analytical problem, and T. D. Yensen, on a new method of determining carbon in iron, consisting in condensing the carbon dioxide produced in liquid air and afterwards evaporating the solidified carbon dioxide in an evacuated space, the pressure produced allowing determination of the carbon in the specimen to 0.001 per cent; L. T. Richardson, on the influence of enclosed slag on causing corrosion of iron, showing that it has practically no influence; Langdon and Grossman, on the effect of sand-blast cleaning and acid pickling on the properties of steel, showing a decided decrease of its resistance to rapid alternating stresses; C. H. Brace, on the details of producing calcium electrolytically on a commercial scale, in a special form of fused-salt electrolyzing apparatus; G. J. Sargent, on electrolytic chromium plating, showing how deposits up to one centimeter thickness have been obtained; Mathers and Sowder, on bronze plating, describing two baths which work industrially; Hartman, Hougen and Kobler, of the Carborundum Company, on the resistance of twelve different special refractory materials to spalling, as tested by spraying when hot with cold water, and to abrasion, as tested when hot by grinding against a cold carborundum wheel. Several of the above papers led to lively discussion, particularly that on the corrosion of iron.

After this session, many of the visitors were guided through the magnificent new buildings of the Institute, while a considerable number stayed behind discussing with the Electric Furnace Association the training of men for running electric furnaces. This topic was discussed with great fervor until it was time to adjourn for dinner.

In the evening, Arthur D. Little, Inc., was host to the Society at its model industrial research laboratories in Cambridge. The museums, library, laboratories and semi-commercial plant in the basement were admired by a gathering which literally filled the building. Later, there were speeches and singing and a good deal of fun, with unlimited smokes, and Professor Armstrong, of the Institute, entertained most charmingly with a pictorial account of hunting with a camera in the wilds of New Brunswick. He delighted and enthused his audience by his breezy account of a most fascinating summer vacation.

Friday was set for joint sessions with the American Institute of Electrical Engineers. The program was a morning session with a Symposium on Electrically Produced Alloys, an afternoon trip to the General Electric Works at Lynn, an informal subscription dinner, followed by an evening session with a Symposium on Power for Electrochemical Purposes. President Bancroft was chairman at the morning session, and President Townley of the Electrical Engineers, in the evening. The 250 electrochemists, together with about 150 electrical engineers, crowded the meeting place—the Swiss Room of the Copley Plaza Hotel—to its full capacity, discussion was active, and the occasion was indeed a notable one.

At the morning session, in the Symposium on Electrically Produced Alloys, the following papers were read and discussed: H. E. Howe, a review of the fundamental problems in alloys research, particularly reciting the physical and chemical data which are needed for thoroughly studying alloys and alloying phenomena; R. J. Anderson and C. B. Gibson each discussed the broad outlines of the ferro-alloy industry, its rise and present commercial importance, and the technique of the general problem of producing ferro-alloys; B. D. Saklatwalla described the ferrovanadium industry, giving occasion for some pungent discussion of the limits of supply of vanadium and its commercial exploitation; F. A. Raven described the physical properties and chemical uses of ferrosilicon; E. S. Bardwell, ferromanganese; Alcan Hirsch, ferrocerium; R. M. Major, nickel chromium and similar alloys; R. C. McKenna, on producing high tungsten high-speed steel in the electric furnace, resulting in considerable discussion of the best form of electric furnace for getting a good mixture of these slowly alloying metals; E. Haynes, on cobalt-chromium alloys, known as stellite, used as high-speed cutting tools and for surgical instruments; T. D. Yeusen, on the magnetic and electric properties of iron-nickel alloys; Hunter and Bacon on similar properties of iron-titanium alloys. Finally, C. F. Harding related his experiments in fixing the nitrogen of the air by a silent discharge process which is at present of very low efficiency (one per cent) but which contains the promise of better things.

The trip to Lynn was made in eight electric cars, directly from and returning to Copley Square, both societies being invited guests of the General Electric Company. A printed itinerary gave all the details of the visit with great accuracy, and it was carried out according to plan with military precision. While duly impressed by the magnitude of the Lynn plants, some of the more critical visitors were not as favorably impressed by the details of execution of the work in some parts of the plants; the Heroult electric steel furnace, however, appeared to be casting steel dead—melted "to the queen's taste;" this operation was given unstinted commendation.

The informal dinner was attended by about a hundred and fifty, and was graced by the presence of our life-long friend, Professor Elihu Thompson.

The evening session was almost a crush. The Symposium on Power for Electrochemical Purposes was calculated to draw out every electrical engineer and every electrochemist within possible reach of Boston. Chairman Townley divided the program into three groups, *viz.*, papers treating on the general question, discussion of specific electric furnace requirements, and presentation of the advantages of specific power sites. In the first class came the following: J. L. Harper, discussing the general requirements of power by electrochemical industries of various kinds; E. A. Wilcox, on the central station man's view of electrochemical customers and their requirements; A. Smith, on abuse of power demands by electric furnace operators, in particular the necessity of controlling excessive surges on the lines. In the second class, H. L. Hess discussed the requirements of electric steel furnace plants; H. A. Winne the use of reactors on electric furnace circuits to reduce the momentary surges or peaks in the power demands; J. A. Seede, on automatic controllers for regulating arc furnace electrodes so as to stabilize the current. In the third class of papers, C. T. Maynard described the power available at Rumford Falls, Maine, only two hundred miles from Boston; F. F. Fowler, the water powers of the Pacific Coast, developed and potential; J. W. Beckman, the power developments of Norway and Sweden, showing how far these countries have out-distanced the United States in developing their power for electrochemical industries.

The Saturday morning session in the new Lecture Hall at Harvard University was lively and interesting. Professor T. W. Richards—"Atomic Weights" Richards—gave the visitors a hearty greeting. The proceedings included the following: J. W. Richards—"Metallurgical Calculations" Richards—described the Söderberg self-baking, continuous electrode, which is already extensively used in Europe and is being installed on some ferrosilicon furnaces at Anniston, Alabama; C. A. Keller's paper on synthetic, electric-furnace pig iron, described the great importance this product attained in France during the war, in utilizing steel turnings and producing cast-iron shells; E. F. Kern described experiments on reducing manganiferous silicate slags in an electric furnace to silico-spiegel; P. B. Short, a step-induction regulator of new form for electric furnaces; C. J. Weed, the general application of the electric furnace to metallurgy; L. B. Lindemuth described in detail the position of the electric furnace in manufacturing steel, concluding that it is the most flexible and most generally useful of all steel-making apparatus; H. M. St. John, on the evolution of the electric brass furnace. Some statements in the last paper as to advantages and power required for melting brass were questioned by Mr. Winder, giving rise to a very lively interchange of opinion between Messrs. Gillette, Baily, FitzGerald, Hering, Richards, and others, which, in general, substantiated the statements in the paper.

After the session, Professor Richards invited those present to inspect the Gibbs Research Laboratory, which opportunity was eagerly accepted. Lunch followed at the Harvard Union, and then a visit to the Huff Electrostatic Separator plant at Arlington closed the program. The visitors found the last item very instructive and interesting.

Thus Boston and the Electrochemical Society came together for the third time, to their mutual profit and advantage.

LEHIGH UNIVERSITY
SOUTH BETHLEHEM, PA.
April 13, 1920

J. W. RICHARDS

CALENDAR OF MEETINGS

American Pharmaceutical Association—Annual Convention, Washington, D. C., May 6 to 8, 1920.

Society of Cotton Product Analysts—11th Annual Convention, Grunewald Hotel, New Orleans, La., May 10 and 11, 1920.

National Foreign Trade Council—Convention, San Francisco, Cal., May 12 to 15, 1920.

National Fertilizer Association—27th Annual Convention, White Sulphur Springs, W. Va., week of June 21, 1920.

American Institute of Chemical Engineers—Semi-Annual Meeting, Montreal, June 21 and 22; Ottawa, June 23; Shawinigan, June 24 and 25; La Tuque, June 26, 1920.

Sixth National Exposition of Chemical Industries—Grand Central Palace, New York, N. Y., September 20 to 25, 1920.

NOTES AND CORRESPONDENCE

FRENCH GAS WARFARE[1]

Little by little the mysteries of the great battle are being cleared up. Soon all the secrets will be known. To-day those of the murderous gas warfare are disclosed by Colonel Vinet, head of the office of chemical research at the Ministry of War.

Our enemies first used this barbarous weapon on April 22, 1915, on the Belgian front between Bixschoote and Langemark. At five o'clock in the evening, a heavy cloud of greenish vapor appeared over the German trenches and, pushed along by a light wind, covered the French lines. The assaulting waves followed. An entire division of the tenth army was overcome. Our men were seized with violent coughing fits and suffocated. Many held firm but paid for their resistance with their lives.

Germany had once more flagrantly violated the laws of war. On July 22, 1899, at the Hague she had indeed signed the international convention prohibiting combatants to "spread asphyxiating or poisonous gases."

This attack most evidently took us by surprise. We had to improvise everything. The task was pressing. We had first of all to seek the means to protect our soldiers against these poisons, then give them the means to retaliate.

M. Kling, director of the Municipal Laboratory of the City of Paris, was hurriedly called to the front, and after a quick survey gave the preliminary instructions with decided farsightedness. The means at hand had to be used—wads of cotton saturated with hyposulfite of soda, ordinary goggles to protect the eyes. An appeal was then sent to the chemists and the work was soon organized.

A commission for chemical research was created, happily realizing the importance of its role, and jostling a little the established bureaucrats who were a little wary of these things which they had not foreseen. Every source was utilized, and the young school of French chemistry showed itself equal to its task. The Pasteur Institute, the School of Pharmacy, the Sorbonne, the College of France, the Conservatory of Arts and Trades, the Faculty of Medicine, all coöperated with ardor in the necessary research work.

Three sections were established: Studies on the front, directed by M. Kling; studies of means of offense, directed by Professor Mouren; and studies of means of protection, directed by Professor Vincent. Intimate relations were also established with general headquarters, which had started a gas warfare service, and had nominated "officers, army chemists." In 1917 this service became interallied, and soon we were ready for both attack and defense.

Germany, in April 1915, had employed simple liquid chlorine escaping from metallic cylinders in which it had been compressed. In June, bromine first put in its appearance, being used in projectiles fired from mine throwers. It was from this time on that gases were used in artillery projectiles. The first serious use was in the Argonne, at the Bois de la Gruerie. Successively, new compounds, of which formaldehyde and chlorine were generally the bases, were used by the enemy. A salvage service allowed us to make investigations very quickly so as to determine the exact nature of these products, their physiological action, and to deduce the therapeutics and the means of effective protection.

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[1] Translation of an article by Lucien Chassaigne in *Le Journal*, Paris, February 24, 1920.

These last arrived at a fine degree of perfection. Our soldiers, wearing their masks, could in the last months of the war remain without inconvenience several hours in an atmosphere containing a high percentage of poisonous gases. Horses, dogs, and carrier pigeons, all had their protective devices.

From September 1915 to September 1918, 12,400,000 masks of different models were manufactured and delivered. From August 1915 to April 1916, 10,000,000 pairs of goggles were also delivered.

The effort to find means to retaliate was no less active. Beginning in September 1915, during the Champagne offensive, we used again the German shells loaded with tetrachlorosulfide of carbon, the only product which we had in sufficient quantities.

Messrs. Urbain and Lebeau then invented a gas with hydrocyanic acid base, calling it "Vincennite," which produced instant mortal action, but which our chiefs through an excess of humanitarian scruples, which were indeed superfluous, decided not to employ. The same decision was arrived at for phosgene, used in the beginning of the Battle of Verdun in February 1916, and which produced a panic which is recorded in the German orders of the day.

The chemists, not discouraged, then turned their efforts towards other products of chlorine or formaldehyde. Finally the choice fell on a product which the Germans had first used in July 1917 at the Battle of Ypres, and which was called for that reason "Yperite," and which is chemically a sulfide of dichlorethyl. This possesses both toxic and blistering qualities.

The manufacture, despite the great difficulties and the dangers which it entailed, was pushed fast. Eleven factories made the necessary chlorine, and up to the armistice had produced 24,000 tons. In the seven months, from April to November 1918, 2,172,334 shells for the "75," 90,810 for the "105," and 142,035 for the "155" had been loaded with yperite.

In all, there had been loaded and fired against the enemy 13,193,000 "75" shells, 3,930,000 heavy shells and trench bombs, and 1,140,000 grenades loaded with gas. We have, besides, ceded 8,000 tons of asphyxiating gases and over a million loaded projectiles to our allies.

These figures are enough to show what a formidable effort was made by our French scientists and manufacturers, an effort of which they may be justly proud, and how well merited was the glorious citation given by Marshal Petain to the chemical services in the war.

CHEMICAL PREPAREDNESS

Editor of the Journal of Industrial and Engineering Chemistry:

Some time ago you gave a talk before some of the chemists of our company assembled in the library. At that time it occurred to me that in spite of receiving encouragement from such men as yourself to keep up our good work, there has been one phase of the general subject of patriotic protective activities not generally considered.

It is doubtless true that as a body of highly trained scientists the American chemists can easily adapt themselves to possible war-time activities, but most of us are really very far from knowing just what we can best do in an emergency. What a chaotic condition is bound to follow when a few thousand men are all suddenly attempting to produce something new and to learn how to do it at the same time!

To parallel the general agitation for universal military training, why should not the American Chemical Society and the large chemical industries get behind the development of a valuable system of peace-time education of their chemists for the pursuit of definite, coördinated and specialized activities in times of possible war? How many of us know anything definite about the manufacture of phenol, picric acid, ethylene, mustard gas, formaldehyde, acetone or wood alcohol, nitrogen fixation, or about large-scale work upon such fundamental processes as nitration, sulfonation, etc., to say nothing of many other technical processes, doubtless of great war-time importance?

It has occurred to me that the American chemical industry might in part repay the country for its many recent advancements if in peace-time in connection with the Government it should adopt a policy of lending its chemists two weeks each year for the purpose of pursuing special studies in "chemical war technology." A so-called "Chemical War College" would in fact be more of a university with its various specializing "colleges" made up of the laboratories and plants of actually functioning industrial plants in various parts of the country. If the chemists were to be loaned the Government then the Government might pay traveling expenses and any peculiar living expenses necessarily incurred by the "war technology" student during his course of training. It would not be many years before we would have in this country an army of chemists each of whom would know exactly what his duty should be, where he should go, with what he would have to work, and how to go about his task in any emergency. These men should be classified and their names and records kept on file, each being subject to emergency call for technical or scientific service at proper salary.

Would it not be worth while to give this matter some discussion in the columns of the Journal?

National Aniline & Chemical Co.
Buffalo, N. Y., April 3, 1920

C. A. Lyford

DECENNIAL CELEBRATION FOR THE FOREST PRODUCTS LABORATORY

The Madison Association of Commerce and Forest Products Laboratory have made preliminary arrangements for the celebration at Madison of the tenth anniversary of the opening of the Laboratory. Present plans call for a two-day meeting during the latter part of June, with addresses by men of national reputation in science and industry, a banquet, tours of inspection through the laboratory, informal discussions, and various forms of entertainment. Detailed arrangements will be announced later.

The Forest Products Laboratory is a branch of the United States Forest Service, established in 1910 in coöperation with the University of Wisconsin, and is a consolidation of a number of testing laboratories and other units of the Forest Service which had been located at various points throughout the United States. It is engaged principally in industrial research on problems connected with the manufacture and use of forest products, including beside lumber, posts, poles, ties, and similar products, pulp and paper, naval stores, hardwood and softwood distillation products, and other chemicals and pharmaceuticals. At the present time the laboratory employs about 200 people and occupies five buildings in whole or in part.

AMERICAN FELLOWSHIPS IN FRENCH UNIVERSITIES

The Society for American Fellowships in French Universities offers each year for open competition among graduates of American colleges and other suitably qualified candidates, 25 fellowships to encourage advanced study and research in French universities. Fellowships of the annual value of $1,000 are granted for one year and are renewable for a second year. Application blanks and further information may be obtained from the Secretary, Dr. I. L. Kandel, 576 Fifth Ave., New York City.

FIRE CAUSED BY YELLOW PHOSPHORUS

Editor of the Journal of Industrial and Engineering Chemistry:

Recently two notes appeared in your JOURNAL about fires caused by yellow phosphorus. In this connection I wish to relate a similar occurrence in our building. All stock chemicals of combustible nature are kept in a fireproof vault which is arranged with shelves made of concrete. The vault is heated with a steam radiator regulated to 55° F. with a thermoregulator. On the evening of February 12, 1920, the steam pipe in the vault burst and the escaping steam melted the yellow phosphorus in the cans and bottles. One bottle containing 3 lbs. of phosphorus broke and the molten phosphorus being on the top shelf, dripped down and ignited. The fire caused only slight damage as it was soon extinguished with sand.

Whenever yellow phosphorus is received in cans it should be immediately transferred to glass-stoppered bottles containing water. Such glass containers should be placed in pails or other receptacles containing water and these in turn imbedded in sand. The container should always be kept on the floor and never on shelves. Periodic inspection of combustible substances of this nature will help to avoid future fires.

ALEXANDER LOWY

SCHOOL OF CHEMISTRY
UNIVERSITY OF PITTSBURGH
PITTSBURGH, PA., March 18, 1920

WASHINGTON LETTER

By J. B. McDONNELL, Union Trust Building, Washington, D. C.

Caught in the cross currents of politics, filibuster and straight out-and-out opposition to its provisions, the dye bill is still before the Senate awaiting action.

The last month has seen but few favorable developments of importance in matters of keen interest to the chemical world which are pending in Washington. The delay in action on the dye bill promises to be lengthy and the chances of failure to get action this session are growing. The army reorganization bill, appropriation bills, peace resolution, and perhaps the soldier bonus measures will all get right of way in the Senate over the dye bill, under present plans.

An effort may be made by Senator Watson to get the measure up within the near future, but whether he will try sufficiently hard to succeed will depend largely upon the result of a conference which he is to have with Senator Penrose, chairman of the Finance Committee, at the latter's home in Philadelphia in the near future. Senator Penrose, who has been absent for several months in Florida because of ill health and only recently returned to Philadelphia, is a high protectionist and, of course, in favor of protecting the dye industry, but he has not given any opinion as to the merits of the measure the committee reported out. It is to get his support of the committee measure and have him exert his very powerful influence on the Senate to remove much of the obstruction tactics that the conference has been decided on.

A peculiar situation has developed among the Republicans. Western senators, through a filibuster which showed itself on the floor when the bill enjoyed its fleeting consideration of a day, just prior to the taking up of the Treaty by the Senate for the second time, have succeeded in forcing the Finance Committee to report out tariff measures it had been determined to "smother" for this session. Since then, they have been at work trying to assure action on the floor on these measures and have nsed obstructionist tactics against the dye bill as a means of bringing pressure to win their point.

Several amendments to the bill are pending. The United States Tariff Commission in a report made to the Finance Committee on the Moses amendment criticizes it and states that it is unworkable in certain of its provisions. The Moses amendment would eliminate the embargo provisions of the committee bill and substitute therefor a system of special tariffs. It is practically an anti-dumping measure. Senator Keyes, also of New Hampshire, has introduced four amendments to the committee bill, upon the assumption, however, that the bill will be adopted without very material changes. His amendments are designed to afford more certain and greater protection to the dye consumer by changing the phraseology of the bill in places.

Senator Thomas, Democrat, of Colorado, has proposed as an amendment to the dye bill a measure imposing a tax equal to one hundred per cent on all political contributions of more than a thousand dollars. He has attempted to get action on this measure several times without success. He has been accused of indulging himself in sarcastic humor in this move. Needless to say, the dye bill has been the target of many charges hurled by opponents, who charge that possible campaign contributions have had the effect of enlisting supporters. It is also needless to say that charges of "lobby" and the crew of additional charges and innuendoes that usually accompanies the first, have been made in connection with other tariff measures pending, few of them escaping.

Favorable report also has been made by the Finance Committee on Senator Smoot's anti-dumping measure. It has been suggested that this be made an amendment to the dye bill, but plans were changed and it was reported as a separate measure. While it is not proposed as a substitute for any section of the dye bill, it is interesting to note that Senator Smoot several times has expressed the opinion that anti-dumping legislation, supplemental to a high protective tariff, would be adequate to protect the dye industry. Although not an ardent supporter of the committee bill, Senator Smoot is not radically opposed to it, however, and will support it when it comes to a vote, according to those in charge of the bill.

As the situation stands at the present time the outlook for action on the bill in the near future is dark; while chances of action on the laboratory and scientific instruments bill are considerably less at this session. The same is true of other tariff measures. Only strong pressure upon members of the Senate to convince them of the necessity of enacting legislation to protect the industry can bring any action, unless the Penrose-Watson conference results in the strong support of the former. There are many senators who would vote for the bill if brought up for action, but the fact that we still are technically at war, with war-time restrictions in force, has been a potent argument in the hands of those Republicans who are opposed to any tariff legislation until after election.

The Senate at the present time is engaged in consideration of the army reorganization measure, which was passed recently by the House. Establishment of the Chemical Warfare Service as a separate department of the Army was provided for in the bill as it passed the House, and although the Senate has not yet acted finally on the provisions of the bill, it also will accord to this important warfare machinery the recognition it should have by making it a separate department, instead of placing it as a sub-division of another department as was proposed by General March, Chief of Staff.

Following hearings which brought scientific and technical men from all over the country to testify before the committee, the House passed the Nolan bill providing for reorganization of the United States Patent Office. This measure is now pending in the Senate Patents Committee of which Senator Norris is chairman. The bill provides for a general reorganization of the patent office, and increases the pay of the staff so as to prevent complete disintegration through resignations. Hearings were held on the bill on April 8, but no action was taken by the committee at that time, because of lack of a quorum. Senator Norris is now in Nebraska and is expected to return here the latter part of April. Present plans are for the prompt calling of the committee and an immediate favorable report to the Senate, where it is proposed to press it for passage at this session.

St. John Perret, chief of the War Trade Board Section of the Department of State, has left here and is now in Europe, where he is acting as the representative of the United States in the allocation of the German dyestuffs through the allied commissions provided for in the Treaty.

Latest official advices are to the effect that there is a prospect of the dock strike, which has tied up shipping at Amsterdam and Rotterdam for many weeks, being broken. Officials state that practically all of the dyes obtained from Germany through the reparations commission and under the option obtained by Dr. Charles H. Herty, from the German chemical cartel, are now in Rotterdam awaiting shipment. They have been there for several weeks, arriving just about the time the strike was begun. Shipping has been paralyzed however and it has been found impossible to move them. Once the strike is ended the barrier will be removed and the dyes will come forward to this country. Only a small percentage of the dyes were returned to the German factories because of failure to come up to the standards required, advices state.

In its program of economy, the keynote of which has been cutting of appropriations allowed Government departments, Congress has severely cut the appropriations allowed the Bureau of Standards. The House, in cutting the estimates presented by the House, pruned so well that the appropriation allowed is less than sufficient to maintain the present work of the Bureau. The Senate refused to materially increase the House appropriations. This will mean that the Bureau cannot carry out some of the plans for extending the work and in some instances must cease work it is now doing.

April 14, 1920

INDUSTRIAL NOTES

The Bureau of Mines reports the results of investigations on electric sparking in mines from lightning. A remarkable explosion of fire-damp was recently caused by a discharge of lightning at the Sitalpur coal mine, India, and numerous accidents have been caused by lightning entering by shot-firing wires. Suggestions are made as to precautions to be taken in wiring, in order to prevent such accidents.

Cibucao wood, which is imported from the Philippines to China, is largely used in the preparation of dyes for coloring cheap papers such as those used in the manufacture of fire crackers and cheap stationery. The Chinese process of extracting the dye is very crude and wasteful, but the business is closely controlled by a strong syndicate which regulates the value of the manufacture and the price of the product.

The Bureau of Mines report on Petroleum Refineries in the United States indicates that the petroleum refinery capacity of the United States is considerably overbuilt. Refineries now have a total rated capacity over 50 per cent in excess of the refinable oil supplies, and when refineries now being constructed are completed the excess may reach 80 per cent. In 1919 the oil runs were 361,520,153 barrels of crude oil, or 990,466 barrels per day.

The attar of rose production by Bulgaria has shown a heavy drop since the First Balkan War in 1912, the production falling from more than 126,800 oz. in 1912 to 52,000 oz. in 1919, with a probable further decrease in 1920. The acreage planted to roses has decreased about 25 per cent in this time. During the war large stocks remained unsold in Bulgaria until early in 1919, when a considerable part of the stock was sent to the United States in exchange for flour. It is estimated that the present available stock in Bulgaria hardly exceeds 50,000 ounces.

A joint Army-Navy Board has been created by the Secretary of War and the Secretary of the Navy for the purpose of coordinating the various helium gas activities. The Bureau of Mines of the Department of the Interior has been invited to have a representative meet with this board.

Representative Graham of Illinois, chairman of the Committee on War Expenditures, which is investigating the government's nitrate and explosive manufacturing operations, recently told the House that the Nitro explosive plant near Charleston, W. Va., which cost the Government $70,000,000, has beens old to the Charleston Improvement Co. for $8,550,000, payable in installments in about 10 years. The company, Representative Graham said, is holding the property for the purpose of investment and speculation.

The Far Eastern Division of the Bureau of Foreign and Domestic Commerce reports that the outlook for American dyes in Japan is good. American dyes do not suffer in manufacture on account of the humidity of the climate, which prevents effective crystallization in the dye products of some countries.

Tests made years ago at the Forest Products Laboratory indicated that sodium fluoride might be successfully used as a wood preservative because it had high toxicity, was not injurious to metal, and was convenient to handle. Tests extending over 5 years on sap-pine ties used in a mine in Birmingham, Alabama, and on red oak ties in the tracks of the Baltimore and Ohio Railway Company show that ties treated with sodium fluoride remain in as good condition as those treated with zinc chloride, both showing very little deterioration. Ties treated with creosote were in still better condition, while untreated ties were in various advanced stages of decay.

The Senate has passed the bill authorizing the Federal Trade Commission to administer inventions for public welfare.

The National Research Council has received a gift of $10,000 from the Southern Pine Association to pay for the incidental expenses of a scientific study by a number of investigators, under the advice of the Research Council's special committee on forestry, of the re-growth of trees or cut-over forest lands, with the aim of determining the best forestry methods for obtaining the highest productivity.

The United States Civil Service Commission announces a competitive examination for analyst in the Bureau of Mines, Pittsburgh, Pa., at $1,200 to $1,500 a year open to both men and women. Ability to make routine analyses of coal, calorimetric experiments, and analyses of ores is required. Applicants must be high school graduates and have had three years' analytical experience in a chemical laboratory, or have had three years' college training which included quantitative analysis. Applications must be filed with the Civil Service Commission, Washington, D. C., on or before May 11, 1920.

The United States Civil Service Commission announces an examination for metallurgist at the Engineering Experiment Station, Naval Academy, Annapolis, Md., at $7.60 per day. Applicants must be college graduates who have majored in chemistry, engineering or metallurgy, and have had one year's experience in the use of the microscope in the examination of metals. Applications must be filed with the Civil Service Commission, Washington, D. C., on or before May 11, 1920.

The United States Civil Service Commission has announced an examination for surveillance inspector in the Ordnance Department at Large, at $1,600 to $2,400 a year. Appointees whose services are satisfactory may be allowed the temporary increase of $20 a month. The duties of appointees will be general supervision of storage and testing of smokeless powder, high explosives and loaded ammunition, making stability tests on smokeless powders and high explosives, and inspection of explosives in storage. Graduation from a standard high school and two years of experience with smokeless powder and explosives are required. Applications must be filed with the United States Civil Service Commission, Washington, D. C., by May 11, 1920.

The specifications recommended by the Inter-Departmental Committee for the Standardization of Paint Specification in the purchase of paint for government use show two significant features: the recognition by paint technologists of the increasing importance of zinc oxide, and the latitude of the specifications. Less than ten years ago no zinc oxide was used by the Government except in the navy and lighthouse service, while now battleship gray pigment is 60 per cent zinc oxide.

The *Technical Review* describes investigations recently made in Switzerland on the use of acetylene as a motive power for automobiles. Two-stroke, four-stroke and Diesel engines were used, with a mixing valve which allows for the variation of the amount of air to be added to the gas. Comparisons of a motor using gasoline and acetylene are given. With acetylene the motor is less liable to overheat and the cylinders and valves keep unusually clean. Oil consumption is heavy when pure acetylene gas is used, but if a small amount of warm water is drawn into the cylinders in the form of a spray, the consumption is less than with gasoline.

Sixteen new companies were chartered during the month of February 1920 for the production and distribution of chemicals, with a total capitalization of more than twelve and a half millions.

The Bureau of Mines has issued a report on the motor gasoline situation, embodying the results of investigations of the motor fuel supply of the United States. The number of automobiles in service increased about 1700 per cent from 1909 to 1918, while the production of gasoline increased 560 per cent, and the production of crude oil only 95 per cent. Because of the great demand for kerosene, it is unlikely that the quantity of gasoline can be increased by making it less volatile than now. The extraction of gasoline from natural gas is approaching its maximum. The supply of fuel oil from which gasoline may be obtained by cracking is sufficiently large, although the demand for fuel oil has increased rapidly and the price has more than doubled, but the process of cracking is expensive and would be unprofitable without a further increase in the price of gasoline. The use of alcohol as a motor fuel will probably increase, as well as the use of benzene produced from coal tar. The solution of the problem will probably be found in the designing of an automobile engine which will use fuel oil satisfactorily, since this will be the most efficient way of using fuel oil, and the supply of motor fuel will be limited only by the total supply of fuel oil.

The Bureau of Mines, Department of the Interior, has recently issued a complete statement of coal-mine fatalities in the United States during 1919. The report shows a reduction of 10.58 per cent in fatalities as compared with 1918, although there was an increase in accidents due to gas and dust explosions. While the actual number of fatalities is considerably less than in 1918, the ratio on a tonnage basis is slightly higher.

The Bureau of Crop Estimates, Department of Agriculture, reports the area of winter wheat planted in foreign lands as follows: Spain, 9,511,000 acres, or 109 per cent of the 5 year average from 1914 to 1918; France, 11,369,000 acres, or 89.5 per cent of the 5 year average; Roumania 1,321,000 acres, or 28.1 per cent of the 5 year average; British India, 27,429,000 acres, or 85.9 per cent of the 5 year average. The condition of cereals is good.

A National First-Aid and Mine-Rescue Contest will be held under the auspices of the Bureau of Mines, Department of the Interior, at Denver, Colorado, August 20 and 21, with a view toward stimulating the safety movement among the mines and metallurgical plants of the country. Teams from the principal mining companies of the country will participate in the contest for the national championship in first-aid and mine-rescue work, and cups, medals and prizes will be awarded to the winners. Arrangements are being made to hold at the same time and place the annual meetings of the Rocky Mountain Coal Mining Institute, the Colorado Metal Mining Association, the American Mining Congress and other mining associations. Mr. D. J. Parker, of the U. S. Bureau of Mines, Pittsburgh, Pa., is in charge of the arrangements for the contests.

The Bureau of Mines has prepared a report on diatomaceous or infusorial earth, showing its uses, method of preparation, chemical composition of various samples, and distribution of deposits in the United States. Contrary to the general impression, diatomaceous earth is not confined to the western part of the United States, but is well distributed in many eastern states.

Westinghouse, Church, Kerr & Co., Inc., engineers and constructors, have recently been merged with Dwight P. Robinson & Co., Inc., constructing and consulting engineers, of New York City. The new company which will be called Dwight P. Robinson and Co., Inc., will have executive offices at 61 Broadway, New York City.

The American-Scandinavian Foundation has established twenty traveling fellowships, each with a stipend of $1,000 to $1,200, to be awarded to men and women of American birth for technological research and humanistic study in the Universities of Sweden, Denmark, and Norway. Ten students will be sent to Sweden, and five each to Denmark and Norway, for a period of study extending over one academic year. Selection of the fellows will be made by a jury of university professors and technical experts appointed by the Foundation. Further information in regard to the fellowships may be obtained from The American-Scandinavian Foundation, 25 West 45th Street, New York City.

The Pittsburgh Experiment Station of the Bureau of Mines is conducting a series of experiments on automobile exhaust gases in connection with the proper ventilation of tunnels and subways through which automobiles must pass. Tests are made on all sizes of cars and trucks under the various conditions, which are found in actual street use, to determine the amount of carbon monoxide produced. Dr. Yandell Henderson, of Yale University, is determining how many parts of carbon monoxide in 10,000 parts of air may be considered safe for a person to breathe for several hours without any ill effects. It is expected that the test will not only solve the problems of tunnel ventilation, but will be of great value to automobile owners and dealers in furnishing unbiased information on the efficiency of any given machine under particular conditions and on obtaining greater mileage through proper adjustment of the carburetor.

A Chilean Section of the Société de Chimie Industrielle has been organized with forty members. It is hoped to include in this new section every industrial chemist who has studied in France.

In a report made to the Natural Gas Conservation Committee the rapidly diminishing supply of natural gas is being felt keenly by the printing industry of the country, including the manufacturers of ink and paper for books, magazines and newspapers. Carbon black obtained from natural gas is the cheapest and best-known color base for printing inks, carbon paper, and typewriter ribbons, and is also used in the manufacture of phonograph records and automobile tires. Because of the short life of natural gas fields, which prevents the manufacture in one place for a long time, manufacturers of carbon black must follow the opening of all new fields.

The War Department has recently sold the picric acid plant at Picron, Arkansas, to H. C. Couch, president of the Arkansas Light & Power Co., who is understood to represent a group of Little Rock business men. Mr. Couch recently purchased the power plant, the water supply, and the gas supply systems. It is planned to make the plant an industrial center.

Experiments on the manufacture of dyes have been in progress for some time near Copenhagen, and although the results have been kept secret they are understood to be successful. Various intermediate products have already been made, and it is hoped to build up a dye industry which will render Denmark independent of foreign dyes.

The Southern Agricultural Chemical Corporation, subsidiary of the Tennessee Copper and Chemical Corporation of New York, is planning a $600,000 fertilizer factory at Atlanta, which will be one of ten fertilizer plants to be erected by the company in the south.

A new edition of the chart for blending casinghead gasoline and naphtha has been prepared for the Bureau of Mines, Department of the Interior, which provides an easy method of determining the amount of naphtha to be used per gallon of casinghead gasoline to obtain a product of any required gravity. Copies may be obtained on application to the Bureau of Mines, Washington, D. C.

The Vinegar Hill Zinc Co. has purchased from the Government the acid plant near Cuba City, Wisconsin, which was erected during the war, and plans to rush the completion of the plant for the manufacture of sulfuric acid. Production is expected to begin about June 1.

The chemical industry in the Netherlands is reviving in spite of many difficulties which it has to face in the very low rate of exchange, the difficulty in obtaining raw materials, high wages, high ocean freights, and foreign competition.

The recent discovery of a valuable molybdenum steel alloy by a British metallurgist has resulted in an increased demand for molybdenum and an increase in price. Low-grade deposits of the mineral molybdenite are found in Australia, India, South Africa, and Peru. Peru mines are now producing nearly 80 per cent of the world's supply. The mines are being exploited by American capitalists, who export the ores to the United States.

At the recent formal inspection of the new laboratories at University College, London, by Prince Arthur of Connaught, Lord Moulton gave an address on "The Training and Functions of the Chemical Engineer." Another £50,000 is still required for the new chemical laboratories.

At the 1919 meeting of the board of governors of the New Zealand Institute it was decided to establish a fellowship of the Institute, to be limited to forty fellows, based on research or distinction in science. Not more than four are to be elected in any one year until the number is complete, after which vacancies will be filled as they occur.

The growing scarcity of gum camphor and the steadily increasing price has led to an investigation of the production of camphor oils from California sages. The method of recovery by steam distillation is not complicated or expensive. The entire group of oils are recovered together, true gum camphor frozen out, and the remainder separated by fractional distillation. The most prolific source of supply seems to be the desert sage of the western plains.

In a report on the Necessity for Helium Conservation, the Bureau of Mines describes the immense importance of helium for the filling of military lighter-than-air craft, on account of its perfect inertness and extreme buoyancy. At the time of the armistice about 150,000 cu. ft. of helium were ready on the dock for shipment to France. Since the supply of helium is limited to a special type of natural gas which is being consumed for domestic and industrial purposes, the Government is endeavoring to explore the extent of this resource and provide ways for its conservation. The Bureau of Mines Experiment Station at Ft. Worth, Texas, would like to learn of any such gases, particularly "wind-gas," and in appropriate cases will send cylinders for collecting samples for analysis.

O. Friedlander Chemical Co. has been awarded damages of $2,000 in a suit against William H. Knox & Co., Inc. On April 5, 1918, the plaintiff agreed to deliver 50 tons of soda ash to the defendant at an agreed price of $3.20 per hundred pounds. The soda ash was tendered on September 13, 1918, but was refused on the ground that the Government had denied an export license to the defendant and that the price charged was in excess of that allowed by the authorities.

Prohibition of the importation of dyestuffs into British India, which went into effect September 6, 1919, has recently been removed.

PERSONAL NOTES

Mr. Leon R. Whitcomb has resigned as chemical engineer with Hill & Ferguson, New York City, and is now associated with the Refinite Co., of Omaha, Neb.

Mr. R. E. Hardee, formerly with the Florida Cotton Oil Co., Jacksonville, Fla., is at present associated with the Florida Industrial Corporation, Gainesville, Fla., as chemist.

Mr. Ivan P. Tashof, specialist in inventions relating to the chemical, electrochemical, and metallurgical industries, recently announced the opening of an office for the practice of patent and trade-mark law, in Washington, D. C.

Dr. Lawrence T. Fairhall, formerly Major in the Sanitary Corps, U. S. Army, is research chemist with the O'Bannon Corporation, West Barrington, Rhode Island.

Mr. W. F. Rudd, of the department of chemistry, at the Medical College of Virginia, has been elected president of the American Conference of Pharmaceutical Faculties.

Mr. Ernest Jenkins Hoffman, who recently resigned as assistant chemist, U. S. Bureau of Mines, Pittsburgh, Pa., has accepted a position in organic research with W. B. Pratt, Inc., Boston, Massachusetts.

Mr. Douglas E. Scott, who for several years has been in charge of the Experimental Paper Mill of Arthur D. Little, Inc., Cambridge, Mass., has resigned and is now with the United Fruit Co., located at Boston, Massachusetts.

Mr. B. P. Caldwell is now with the Polytechnic Institute, Brooklyn, N. Y., as professor of analytical chemistry.

Mr. J. M. Clark, formerly chief chemist for the Sherwin-Williams Co., is now connected with the Deloro Smelting and Refining Co., Deloro, Ontario, Canada, in the capacity of superintendent.

Mr. J. B. Krak has left the West Virginia Geological Survey and has taken a position with the General Chemical Co., at the Laurel Hill Laboratories, Laurel Hill, Long Island.

Mr. Henry W. Esterwood, formerly with the F. S. Royster Guano Co., Norfolk, Va., as chemist, is at present analytical chemist in the Jackson Research Laboratories of E. I. du Pont de Nemours & Co., at Deep Water Point, New Jersey.

Mr. Gaston J. Levy, who served as Second Lieutenant in the Chemical Warfare Service, at Hanlon Field, France, has accepted the position of chemist with the Sperry Flour Co., Spokane, Washington, and is in charge of their laboratory there.

Mr. Clarence E. Breckenridge, formerly chief engineer for Merck & Co., New York, recently accepted a similar position with Rockwood & Co., Brooklyn, N. Y.

Mr. J. O. Halverson, for the past three years associate in the department of nutrition in the Ohio Agricultural Experiment Station, recently took charge of nutrition work in the Agricultural Experiment Station at Raleigh, N. C.

Mr. E. Olney Herman has resigned as industrial physicist at the Lynite Laboratories of the Aluminum Castings Co., Cleveland, O., and is now in charge of general technical and efficiency matters for the Eureka Company, North East, Pennsylvania.

Mr. F. Rohde has resigned as vice president and general manager of the Palo Company, New York City.

Mr. E. Gorgas Bashore, formerly chief chemist of the Babcock & Wilcox Co., has become a partner of Mr. Cyrus Wm. Rice under the firm name of Rice & Bashore, with offices located in Pittsburgh, Pennsylvania.

Dr. F. W. Zerban, formerly research chemist for the Louisiana Sugar Experiment Station, has accepted a position as research chemist with the firm of Penick & Ford, Ltd., New Orleans, Louisiana.

Mr. Arthur L. Davis has resigned as assistant catalytical chemist at the Fixed Nitrogen Research Laboratory, American University, Washington, D. C., and is now employed as research chemist with the International Coal Products Corp., Newark, New Jersey.

Mr. E. K. Kanet, formerly traveling superintendent of the Wm. F. Mosser Co., Richwood, W. Va., has become research chemist with the Goodyear Tire & Rubber Co., Akron, Ohio.

Dr. F. M. Beegle, formerly chemist for the American Chemical & Manufacturing Co., Norfolk, Va., is now chief chemist for the Glidden Company, Cleveland, Ohio.

Mr. Charles W. Studt, formerly a manufacturing chemist with the Mallinckrodt Chemical Works, St. Louis, Mo., is now chief geologist for the Eclipse Oil Co., Fort Worth, Texas.

Mr. William C. Dowd has left the American Smelting & Refining Co., Pueblo, Colo., where he was employed as chemist, to accept the position of chief chemist at the Austin Plant of the American Radiator Co., Buffalo, New York.

Mr. H. H. Hanson, formerly in charge of the feedingstuffs laboratory of the West Virginia State Experiment Station, is at present state chemist of the State Board of Agriculture, Dover, Delaware.

Mr. L. B. Shipley, formerly chemist and technical representative, in matters pertaining to coal-tar heavy oils, for the Barrett Company, is now associated with the Bernuth Lembcke Co., Inc., New York City, in a similar capacity.

Mr. Oregon B. Helfrich has just received his Ph.D. degree from the Johns Hopkins University and has accepted a position with E. I. du Pont de Nemours & Co., doing research work in the Delta laboratory of that company at Arlington, New Jersey.

Dr. Percy W. Punnett, formerly in the organic research laboratory of the Butterworth-Judson Corp., Newark, N. J., is at present with the Rochester Button Co., Rochester, New York, as chemist.

Dr. R. L. Kahn, formerly associated with New York University and Bellevue Hospital Medical College in the department of bacteriology, recently accepted an appointment as immunologist in the laboratory of the Michigan Department of Health, Lansing, Michigan.

Dr. Donald K. Tressler has resigned as research chemist of the varnish department of the Acme White Lead and Color Works, Detroit, Mich., to accept an industrial fellowship with the Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

Dr. John Charles Hessler has been appointed assistant director of the Mellon Institute of Industrial Research of the University of Pittsburgh. Dr. Hessler, who is now serving as president of James Milliken University, Decatur, Ill., will enter upon his new duties at the close of the present academic year. As a member of the administrative staff of the Institute, Dr. Hessler will be in supervisory charge of certain of the researches in organic chemistry, a field in which he has specialized during the past twenty years.

Dr. J. J. Elbert, a technologist with the American Cyanamid Co., New York City, and a member of both the American Electrochemical Society and the American Chemical Society, died suddenly at his home in Tuckahoe, N. Y., on February 27. He was a graduate of Massachusetts Institute of Technology in chemical engineering, and of the University of Berlin.

Mr. Fred Olsen has resigned as chief of the research department of the Aetna Explosives Co., and is now attached to the Explosives Section of the Ordnance Department, Washington, D. C., directing various researches in explosives.

Mr. W. G. Koupal, a recent graduate of the University of Illinois, Urbana, Ill., is at present with the Pittsburgh Plate Glass Co. as a chemist in their research laboratories at Creighton, Pennsylvania.

Mr. Morris Schrero, formerly in the technology department of the Carnegie Library of Pittsburgh, Pittsburgh, Pa., has accepted a position as associate chemist in the research division, department of technical control, of the American Writing Paper Co., Holyoke, Massachusetts.

Dr. Lathrop E. Roberts, who received the degree of Ph.D. last December at the University of Chicago, Chicago, Ill., is now assistant director of technical control, American Writing Paper Co., Holyoke, Massachusetts.

Mr. W. B. Burnett, formerly in charge of the science work at the Masonic Home, is serving as assistant on the inorganic staff of the University of Illinois, Urbana, Ill., where he is at the same time doing graduate work.

Mr. J. Wm. Barker, recently a student at Kansas State College, Manhattan, Kans., has accepted a position as control chemist in the Marysville, Kansas, mill of the Larabee Flour Mills Corp., Kansas City, Missouri.

Mr. Frederick R. Ward has left the American Manganese Manufacturing Co., Dunbar, Pa., where he was employed as chief chemist and is now connected with the Tennessee Manganese Co., of Cleveland, Tenn., in the same capacity.

Mr Arthur L. Day has changed from the Corning Glass Works, Corning, N. Y., to the Geophysical Laboratory, Washington, D. C.

Mr. Ralph E. Canfield, formerly with the American Nitrogen Products Co., at their nitric acid factory in Lake Buntzen, B. C., Canada, is now chemist for the Crown Willamette Paper Co., at their Camas, Washington, plant, where the laboratory work for all the paper mills of the company is now being centralized.

Mr. T. B. Peters, a recent graduate from the Pennsylvania State College, has accepted a position in the operating laboratory of E. I. du Pont de Nemours & Co., at their plant in Arlington, New Jersey.

Dr. David Klein has resigned as associate professor of biochemistry in the Johns Hopkins University School of Public Health and Hygiene, and has taken a position with the Hollister Wilson Laboratories, Chicago, Ill., as director of research and control laboratories.

Mr. G. A. Brewster, formerly chief chemist and metallurgist of the American Steel Foundries, has taken a position as metallurgist for the Arco Steel Department of the American Radiator Co., Buffalo, New York.

Mr. H. K. Baumgardner, until recently research chemist for the Crown Cork and Seal Co., Baltimore, Md., is now conducting researches for the H. I. Roosen Co., Brooklyn and New York, manufacturers of printing and lithographic inks and dry colors.

Mr. J. R. Marston, formerly superintendent of lead refinery with the Cia Minera Fundidora y Afinadora, of Monterrey, Mexico, has recently undertaken some research work for the United Verde Copper Co., Clarkdale, Arizona.

Dr. Henry Arnstein has resigned as technical director with the Cereal Products Refining Co., and has opened consulting offices devoted to the manufacture of various food products, in San Francisco, California.

The Rumford Committee of the American Academy of Art and Sciences at its recent meeting appropriated the sum of $250 to Prof. Julius Stieglitz in aid of the publication of Marie's "Tables of Constants."

Assistant Professor Gerald L. Wendt, of the department of chemistry, University of Chicago, Chicago, Ill., has been appointed associate editor of the *Journal of the Radiological Society of North America.*

Mr. W. K. Buck, formerly in the metallurgical laboratory of the Naval Engineering Experiment Station, Annapolis, Md., has joined the forces of the Aluminum Co. of America, in their technical direction department, New Kensington, Pa.

Mr. Charles A. Stanwick who was honorably discharged from the U. S. Army in July of last year, is at present in the employ of the Western Electric Co., N. Y. C., as electrical engineer. In addition to this Mr. Stanwick is instructor in electrical engineering at Cooper Union Institute, New York City.

Mr. Oliver C. Ralston has left the employ of the Hooker Electrochemical Co., Niagara Falls, N. Y., where he was chief metallurgist, to become superintendent of the Seattle, Wash., station of the U. S. Bureau of Mines.

Dr. Colin G. Fink, head of the laboratories of the Chile Exploration Co., recently lectured to the graduate students of the School of Chemistry, Yale University, on "Industrial Research," and on "The Value of Physical Chemistry to the Organic Chemist."

Associate Professor C. J. Frankforter is in charge of the department of chemistry of the University of Nebraska, Lincoln, Neb. Some new courses in practical chemistry have been introduced by this department and have been working out very successfully since they were opened last September. The department is housed in a very fine new laboratory and the chairman of the chemistry faculty, **Dr. F. W. Upson**, is arranging for courses devoted to chemical engineering subjects. The department has also put in a course in oil and gas which is primarily for geologists.

Mr. J. Roy Haag, previously assistant chemist of the R. I. Agricultural Experiment Station, Kingston, R. I., has become assistant chemist, department of soil investigations, Agricultural Experiment Station, College Park, Maryland.

Mr. W. B. Hicks has resigned as chemist in the U. S. Geological Survey to take charge of analytical research for the Solvay Process Co., Syracuse, New York.

Mr. S. G. Keller, Jr., has severed his relations as assistant superintendent with the Standard Asphalt & Refining Co., Independence, Kansas, to become assistant superintendent of the Empire Refineries, Inc., Ponca City, Oklahoma.

Mr. D. Fay Hosman for the past three years research and consulting chemist for the Blue Valley Creamery Co., Chicago, Ill., has left that firm to become manager of the creamery department of the Scottsbluff Creamery Co., Scottsbluff, Nebraska.

Mr. Andrew Bender, formerly with the Air Reduction Co., as research chemist in their Jersey City laboratory, has joined the Barrett Co., and will be in charge of the control laboratory of their Frankford plant, Frankford, Philadelphia, Pa.

Mr. Ivar Bull Simonsen, until recently connected with the Niagara Smelting Corp., Niagara Falls, N. Y., as metallurgist, is at present with the Tennessee Manganese Co., as metallurgist at their plant in Cleveland, Tennessee.

Mr. Frederick L. Begtrup has left the Metal & Thermit Co., Jersey City, N. J., where he was employed as analytical chemist, and has taken a position with the Niagara Sprayer Co., Middleport, N. Y.

Mr. P. B. Caster, formerly with the Western Sugar Refinery and Spreckles Sugar Co., San Francisco, Cal., has joined the forces of the California and Hawaiian Sugar Refining Co., Crocket, Cal., as assistant to the plant manager.

Mr. James F. Walsh, chemical engineer, and lately Lieutenant in the Chemical Warfare Service, in charge of the charcoal development at the Astoria Plant of the Gas Defense Division, is at present with Wheeler & Woodruff, chemical engineers, of New York City.

GOVERNMENT PUBLICATIONS

By Nellie A. Parkinson, Bureau of Chemistry, Washington, D. C.

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

CONGRESSIONAL COMMITTEES

Coal. House Report 600. 21 pp. February 6, 1920. Mining of coal, phosphate, oil, gas, and sodium on public domain. Conference Report to accompany Senate Document 2775, submitted by Mr. Sinnott.

Dyes and Dyeing. Senate Report 425. 5 pp. February 14, 1920. Importation of coal-tar products. Report to accompany House Resolution 8078, submitted by Mr. Watson.

LIBRARY OF CONGRESS

List of References on Dyestuffs. 186 pp. Paper, 15 cents. Compiled under the direction of H. H. B. Meyer. Contains the chemistry, manufacture, and trade in dyestuffs.

PUBLIC HEALTH SERVICE

The Efficiency of Certain Devices Used for the Protection of Sand Blasters against the Dust Hazard. C.-E. A. Winslow, Leonard Greenburg and E. H. Reeves. Public Health Reports, 35, 518–34. The article describes the dust problem in sand blasting, previous studies of the efficiency of helmets and respirators designed for the protection of the worker in dusty trades, installation and methods used in the present study, results of the present study, and gives a summary and practical conclusions in regard to the protection of sand-blast operators.

GEOLOGICAL SURVEY

Deposits of Manganese Ore in Arizona. E. L. Jones, Jr., and F. L. Ransome. Bulletin 710-D. Contributions to Economic Geology, 1919, Part I. 92 pp. Issued January 29, 1920. Fifty scattered deposits were examined. Some of the deposits are within a few miles of a railroad, but most of them are more than 15 miles distant. No roads have been built to some of the deposits, and from a few of them the ore is packed on animals to the nearest roads. The cost of transporting the ore to the railroad by wagon or automobile truck ranges from 35 to 50 cents per ton-mile. The analysis of the manganese ore from various claims is given.

Deposits of Manganese Ore in Southeastern California. E. L. Jones, Jr. Bulletin 710-E. Contributions to Economic Geology, 1919, Part I. 24 pp. Issued December 30, 1919. The possibility of commercial production of manganese ore in this region is determined by the accessibility of the deposits and the cost of transportation and mining. Water and fuel must be hauled to the camps. All the mining is done by hand and the mining costs are high. The ore is sorted by hand or screened in order to bring it to the required grade. Although it appears to be well adapted to mechanical concentration by wet gravity processes, the lack of water near the deposits precludes the installation of such machinery on the ground, and the expense of hauling the crude ore for considerable distances to water would probably not be justified.

The manganese ore consists of the oxides, of which psilomelane, pyrolusite, and manganite have been determined. Psilomelane is the dominant oxide in all these deposits. Calcite is universally present in the ores, though it varies largely in quantity. Iron oxides are scarce in most of these deposits. Quartz was nowhere observed as a primary constituent of the manganese deposits. No manganese mineral other than oxides was recognized in any of these deposits, but none of the workings had passed through the oxidized zone.

Oils in the Warm Springs and Hamilton Domes, near Thermopolis, Wyoming. A. J. Collier. Bulletin 711-D. Contributions to Economic Geology, 1919, Part II. 12 pp. Issued January 16, 1920.

Preliminary Report on the Chromite of Kenai Peninsula, Alaska. A. G. Gill. Bulletin 712-D. Mineral Resources of Alaska, 1918-D. 31 pp. The amount of ore above sea level at Port Chatham, on the assumption that material containing 10 per cent of chromic oxide can be profitably concentrated, has been estimated at 32,300 tons. Below sea level there may be a much greater amount, as the lower deposits are as a rule richer and heavier than those at higher altitudes. The exposures examined lead to an estimate of 12,600 tons below tide. The amount of chromite in sight at Red Mountain is placed at 195,600 tons. So long as chrome ore containing 40 or 45 per cent of chromic oxide is marketable, it will probably pay to continue the present process of hand sorting. It is estimated that one-half to three-quarters of the available tonnage of chromite in this region would require concentration, and if it is found that ore carrying less than 10 per cent chromic oxide can be profitably milled, the tonnage of available chromite will be much greater than these estimates.

Deposits of Manganese Ore in Nevada. J. T. Pardee and E. L. Jones, Jr. Bulletin 710-F. Contributions to Economic Geology, 1919, Part I. 40 pp. Issued March 15, 1920. Manganese is rather widely distributed in Nevada. In addition to the small amounts that occur in rocks generally it is more or less abundant in many of the metalliferous quartz lodes and in deposits of other types. The classification and general features of the manganese deposits include deposits formed by replacement of country rock by carbonate or silicate minerals that have become partly or completely oxidized; deposits formed by replacement of country rock by oxide minerals; and silicate and carbonate lenses in metamorphic rocks.

Metals and Nonmetals, Except Fuels. F. L. Ransome and E. F. Burchard. Bulletin 710. Contributions to Economic Geology (Short Papers and Preliminary Reports) 1919, Part I. 8 pp. 1920.

Gold, Silver, Copper, Lead, and Zinc in Utah in 1918. V. C. Heikes. Separate from Mineral Resources of the United States, 1918, Part I. 35 pp. Issued March 4, 1920. There was a decrease in 1918, as compared with 1917, in the output of ore and in the production and value of all the metals except silver, as shown by the following table:

Mine Production of Gold, Silver, Copper, Lead, and Zinc in Utah 1917-1918

	1917	1918	Decrease in 1918	1864-1918
No. of producers...	334	251	...	.....
Ore, short tons.....	15,358,481	14,705,718	652,763	.....
Gold[1]............	\$3,355,156	2,949,170	405,986	96,068,503
Silver,[1] fine ounces.	13,479,133	13,455 597	23,536	379,476,124
Copper, lbs	246,674,153	227,169,630	19,504,523	2,189,332,043
Lead, lbs..........	178,521,958	167,008,224	11,513,734	4,142,608,381
Recoverable zinc, lbs.............	21,286,871	18,399,417	2,887,454	210,357,026
Total Value.......	\$99,328,155	86,047,597	13,280,558	1,002,202,934[2]

[1] Includes small placer production.

[2] The total by years to the end of 1913 appears in Mineral Resources for 1913, pt. 1, p 366, 1914.

Mineral Waters in 1918. A. J. Ellis. Separate from Mineral Resources of the United States, 1918, Part II. 37 pp. Issued March 19, 1920. The statistics given refer only to domestic mineral waters that have been sold, imports being excepted. Three uses of mineral waters are recognized—table, medicinal, and in the manufacture of soft drinks. The sources of mineral waters are described, and the mineral water trade in 1918 is reviewed as well as the mineral water trade by states.

Architectural Concrete Stone and Concrete Blocks in 1917 and 1918. G. F. Loughlin. Separate from Mineral Resources of the United States, 1918, Part II. 8 pp. Issued March 16, 1920. The publication was prepared in response to numerous requests for statistical information on the production of artificial stone.

Asbestos in 1918. J. S. Diller. Separate from Mineral Resources of the United States, 1918, Part II. 12 pp. Issued March 20, 1920. Includes an account of the domestic output, varieties and types of asbestos, asbestos in the United States, prices, imports, exports, foreign deposits and production, and the world's production.

The Data of Geochemistry. F. W. Clarke. Bulletin 695, 4th edition. 832 pp. 1920.

Bauxite and Aluminum in 1918. J. M. Hill. Separate from Mineral Resources of the United States, 1918, Part I. 14 pp. Issued March 16, 1920. The quantity of bauxite marketed in the United States in 1918 showed an increase over the production of 1917 of about 7 per cent in quantity and about 11 per cent in value. The production from the Georgia, Alabama, and Tennessee fields in 1918 showed a decrease of 31 per cent, but the Arkansas production showed an increase of approximately 1 per cent. Of the quantity of domestic bauxite marketed in 1918, apparently the producers of aluminum took about 419,043 long tons, the makers of chemicals about 63,896 tons, makers of abrasives about 112,908 tons, and the makers of refractories about 9,874 tons.

The value of primary aluminum produced in the United States in 1918 showed a decrease of about 10 per cent from the value of the output in 1917. The decrease was due very largely to the decline in price of aluminum during 1918 and does not represent a corresponding decline in quantity of output.

Copper in 1917. B. S. Butler. Separate from Mineral Resources of the United States, 1917, Part I. 74 pp. Issued March 13, 1920. The report includes: A summary of statistics of the copper industry in the United States in 1912, 1913, 1914, 1915, 1916, and 1917; an account of the general condition of the industry, including the world's production and consumption and domestic conditions; statistics showing the production, imports, exports, consumption, uses, prices and costs of copper; and a review of foreign production.

BUREAU OF MINES

A Glossary of the Mining and Mineral Industry. A. H. FAY. Bulletin 95. 754 pp. Reprint. Cloth, 75 cents. 1920.

Absorption as Applied to Recovery of Gasoline Left in Residual Gas from Compression Plants. W. P. DYKEMA AND R. O. NEAL. Technical Paper 232. Petroleum Technology 53. 43 pp. Paper, 15 cents. 1920.

Metal-Mine Accounting. C. B. HOLMES. Technical Paper 250. 63 pp. Paper, 10 cents. February 1920.

Metal-Mine Accidents in the United States during the Calendar Year 1918. Compiled by A. H. FAY. Technical Paper 252. 113 pp. Paper, 10 cents. 1920. Includes supplemental labor and accident tables for the years 1911 to 1918, inclusive.

Accidents at Metallurgical Works in the United States during Calendar Year 1918. Compiled by A. H. FAY. Technical Paper 256. 23 pp. Paper, 5 cents. Issued January 1920.

BUREAU OF STANDARDS

Melting Points of Chemical Elements, and Other Standard Temperatures. Circular 35. 4th ed. 2 pp. Paper, 5 cents. Issued December 1, 1919.

Specifications for the Manufacture and Installation of Railroad Track Scales. Circular 83. 35 pp. Paper, 5 cents. Issued January 31, 1920.

Recommended Specification for Basic Carbonate White Lead, Dry and Paste. Circular 84. 10 pp. Paper, 5 cents. Issued December 27, 1919. Prepared and recommended by the United States Interdepartmental Committee on Paint Specification Standardization, August 11, 1919. Basic carbonate white lead may be ordered in the form of dry pigment or paste ground in linseed oil. Material shall be purchased by net weight.

(*a*) DRY PIGMENT—The pigment shall be the product made from metallic lead and shall have a composition corresponding approximately to the formula $2PbCO_3.Pb(OH)_2$. It shall be thoroughly washed after corroding, shall be free from impurities and adulterants, and shall meet the following requirements:

Color—Color Strength—When specified, shall be equal to that of a sample mutually agreed upon by buyer and seller.

	Minimum Per cent	Maximum Per cent
Coarse particles:		
Retained on Standard No. 200[1] screen..	..	None
Retained on Standard No. 325[1] screen..	..	2.0
Lead carbonate........................	65.0	75.0
Total impurities, including moisture......	..	2.0

[1] The No. 200 and No. 325 screens are the same as screens formerly known as 200 mesh and 350 mesh.

(*b*) PASTE—The paste shall be made by thoroughly grinding the above-described pigment with pure raw or refined linseed oil.

The paste as received shall not be caked in the container and shall break up readily in oil to form a smooth paint of brushing consistency. The paste shall consist of:

	Minimum Per cent	Maximum Per cent
Pigment..................................	90	92
Linseed oil..............................	8	10
Moisture and other volatile matter..........	..	0.7
Coarse particles and "skins" (total residue retained on No. 325 screen based on pigment)	..	2.0

Recommended Specification for Basic Sulfate White Lead, Dry and Paste. Circular 85. 11 pp. Paper, 5 cents. Issued January 26, 1920. Prepared and recommended by the United States Interdepartmental Committee on Paint Specification Standardization, September 22, 1919.

Basic sulfate white lead may be ordered in the form of dry pigment or paste ground in linseed oil. Material shall be purchased by net weight.

(*a*) DRY PIGMENT—The pigment shall be the sublimed product prepared from lead sulfide ores, free from impurities and adulterants, and shall meet the following requirements:

Color—Color Strength—When specified shall be equal to that of a sample mutually agreed upon by buyer and seller.

	Minimum Per cent	Maximum Per cent
Coarse particles:		
Retained on standard No. 200[1] screen...	..	None
Retained on standard No. 325[1] screen...	..	0.5
Composition:		
Lead oxide...........................	11.0	18.0
Zinc oxide...........................	..	9.0
Total impurities, including moisture.....	..	1.0
The remainder shall be lead sulfate		

[1] The No. 200 and No. 325 screens are the same as screens formerly known as 200 and 350 mesh.

(*b*) PASTES—The paste shall be made by thoroughly grinding the dry pigment with pure raw or refined linseed oil.

The paste as received shall not be caked in the container and shall break up readily in oil to form a smooth paint of brushing consistency. It shall mix readily in all proportions without curdling with linseed oil, turpentine, or volatile mineral spirits, or any combination of these substances.

The paste shall consist of:

	Minimum Per cent	Maximum Per cent
Pigment....................................	89	91.0
Linseed oil................................	9	11.0
Moisture and other volatile matter	..	0.7
Coarse particles and "skins" (total residue retained on No. 325 screen, based on pigment)............	..	0.5

Metals: Standard Samples Issued or in Preparation. Circular 25, supplement. 5 pp. Issued February 28, 1920. Supersedes all previous supplements.

Recommended Specifications for White Paint and Tinted Paints Made on a White Base—Semi-paste and Ready Mixed. Circular 89. Prepared and recommended by the United States Interdepartmental Committee on Paint Specification Standardization, January 26, 1920.

Prescribes specifications for pigment, liquid, semipaste, and ready-mixed paint, methods of sampling, laboratory examinations of semi-paste and mixed paint, analysis of pigment and reagents employed. It is believed that this specification admits practically all high-grade prepared paints generally available in the United States, and which are therefore obtainable without requiring manufacturers to make up special lots.

Concerning the Annealing and Characteristics of Glass. A. Q. TOOL AND J. VALASEK. Scientific Paper 358. 45 pp. Paper 10 cents. Issued January 31, 1920. Certain methods for determining the annealing range were tested, and the "annealing temperatures" obtained are given for a number of optical glasses. The critical temperature range for these glasses was determined. Some of the methods available for determining the relaxation time were tested. A cooling procedure which proved very satisfactory in the laboratory is discussed.

Estimation of Nitrates and Nitrites in Battery Acid. L. B. SEFTON. Technologic Paper 149. 10 pp. Paper, 5 cents. Issued February 24, 1920.

Determination of Cellulose in Rubber Goods. S. W. EPSTEIN AND R. L. MOORE. Technologic Paper 154. 16 pp. Paper, 5 cents. Issued February 20, 1920. A method is presented which is readily applicable to the determination of fabric in rubber sheeting, raincoat materials, waterproofed fabrics, spread goods, frictioned and calendered fabrics in general.

Cements for Spark-Plug Electrodes. H. F. STALEY. Technologic Paper 155. 10 pp. Paper, 5 cents. Issued February 21, 1920.

Metallographic Features Revealed by the Deep Etching of Steel. H. S. RAWDON AND SAMUEL EPSTEIN. Technologic Paper 156. 24 pp. Paper, 10 cents. Issued March 19, 1920. The method of deep etching of steel by means of concentrated acids was examined in detail. The metallographic features of steel revealed by deep etching are of three general types: Chemical inhomogeneity, mechanical nonuniformity, and physical discontinuities.

DEPARTMENT OF AGRICULTURE

A Pink Yeast Causing Spoilage in Oysters. A. C. HUNTER. Department Bulletin 819. 24 pp. Issued March 10, 1920. Paper, 5 cents.

The Microscopical Examination of Flour. G. L. KEENAN AND M. A. LYONS. Department Bulletin 839. 32 pp.

COMMERCE REPORTS—MARCH 1920

Camphor allotments for January, February, and March, 1920, are as follows: United States, 379,635 lbs.; France, 56,876 lbs.; England, 134,915 lbs. The price per hundred weight has been increased greatly. (P. 1220)

After extensive investigations in Sumatra and the Federated Malay States, the conclusion has been reached that it would not pay the rubber plantations to collect **seed** especially for the purpose of **extracting oil** therefrom unless other oil-bearing seeds could be produced in the same locality. (P. 1221)

Nothing is being done in New Zealand to utilize the **wool scouring waste.** (P. 1221)

Prices of **tin plate** in France continue to rise and available supplies tend to decline. Tin plates of 1 meter and 25, 29, and 33 centimeters in thickness are completely lacking on the market and are greatly needed. (P. 1231)

The difficulties of supply and price of **gasoline** in the British Isles can only be overcome by the discovery of new fields, increased production in and better distribution from existing fields, and the substitution of other liquid fuels for gasoline. Benzene, power alcohol, and coal gas are suggested as substitutes. (Pp. 1236–7)

The production of cooking utensils from **stainless or rustless steel** is reported. (P. 1244)

Conditions in the **petroleum refineries** of Budapest are critical from want of raw material. (P. 1250)

The large **German nitrogen works** producing calcium cyanamide would face immediate ruin were it not for the protection of a syndicate organized under the patronage of the state to maintain uniform prices for nitrogen products. The low exchange also acts as a high tariff on imports into Germany. (Pp. 1251–2)

It is expected that the manufacture of **textile substitutes** will be highly profitable in Germany and strenuous efforts are being made to develop this industry. The production depends upon the availability of large supplies of both alcohol and nitric acid. (P. 1252)

The **German aluminum industry** was overdeveloped during the war when aluminum was used as a substitute for copper in most electrotechnical products. The low exchange value of the mark affords protection to the domestic industry, but under normal conditions the industry would be at a disadvantage as against the aluminum industry of other countries as the German works use brown coal, while other countries use water power. The difficulty of securing raw materials is another source of trouble. (P. 1252)

Another great German war industry is the manufacture of **synthetic rubber.** Whether this industry will continue to be profitable will depend upon the protection afforded by the low exchange value of the mark. (Pp. 1253–4

The **soap making industry** has been revolutionized by the production of a colloidal clay soap. The clay increases the lathering and detergent properties of the soap and by its use the present proportion of fatty acids can be halved. (Pp. 1262–3)

Statistics showing the production of **beet sugar in Spain** during the seasons July 1 to November 1, 1918 and 1919 are given. P. 1263)

A market for **brass and copper** is reported in Argentina. (P. 1267)

The manufacture of **paints** in South Africa promises to become eventually an industry of considerable importance. Almost inexhaustible supplies of earth pigments, ochres, and oxides exist there. Imports of ochres and linseed oil are diminishing. (Pp. 1293–4)

A large stock of **salt** on hand is reported at Cadiz, Spain, due to the scarcity of shipping facilities and extremely high ocean freights. (Pp. 1294–5)

All restrictions on the purchase or sale of **hides, calfskins or kips** in Great Britain and Ireland have been withdrawn, but existing restriction on the export of these commodities will be maintained. (P. 1297)

Italy's rubber industry is reported to be in a favorable condition. (Pp. 1299–1300)

The Venezuelan government has imposed certain regulations in regard to the tapping of **trees producing gums, such as rubber,** balata, etc. (P. 1302)

Statistics giving the final detailed estimate of **India's 1919–20 sesame crop** are given. The condition of the crop is reported to be generally good. (P. 1309)

A French decree of March 2, 1920, prohibits from March 5 the exportation and reëxportation of **coal tar** and **products** obtained direct by distillation of coal tar, except under license from the Ministry of Finance. (P. 1329)

The test of **concrete tanks** used for water storage, undertaken by the Bureau of Standards, has been discontinued because the daily loss has become constant. These tests seem to demonstrate that the 1:2:4 concrete is sufficiently waterproof for this purpose. (P. 1331)

The **French** resources of **iron ore** are described. (Pp. 1356–61)

The British government has placed a fund of £1,000,000 at the disposal of its Research Department to **encourage industries to undertake research.** The Advisory Council for Scientific and Industrial Research has therefore recommended that the fund be expended on a coöperative basis in the form of liberal contributions toward the income raised by voluntary associations of manufacturers established for the purpose of research. The privileges accorded members, the establishment of information bureaus and research companies are described and a list is given of the associations organized and contemplated. The results of any research belong to the association, which will hold them in trust for the benefit of its members. (Pp. 1362–4)

A technical committee has been appointed to study and report upon arrangements on a large scale for the distillation of the **crude petroleum** obtained from the Argentina oil wells with the object of extracting from it light oils and essences such as naphtha, gas oil, and benzine for industrial use. The oil is said to be of a very high quality. (Pp. 1368–9)

The production of **antimony** in the Province of Hunan, China, has fallen off considerably since the close of the war, many smelters having closed down. (P. 1370)

The Bureau of Standards is conducting an investigation with a view to the elimination of **"fish scaling" in enamels** for sheet steel. (P. 1374)

A market for **rubber goods** in the Canary Islands is reported (P. 1385)

Belgium is still in need of the following products to carry on her **reconstruction program:** hematite pig iron, puddled pig iron, semi-steel products, gas coal, mineral substances for the manufacture of chemical and pharmaceutical products and drugs, potassium chlorate, amorphous phosphorus, sesquisulfide of phosphorus, glue, paraffin, and aniline colors. The following products are now ready for export: silver sand, glue stock, precipitated phosphate of lime, white lead, litharge, red lead, blueing, window glass, and sole leather. (Pp. 1399–1405)

The shortage of **Belgian plate glass** continues and there are no prospects of immediate increase. (P. 1425)

The **tanning industry** in Sao Paulo, Brazil, has been established on a secure footing, due to conditions brought about by the war. (Pp. 1429–32)

The Indian Department of Statistics has issued its first forecast of the 1919–20 crop of **winter rape, mustard,** and **linseed oils.** (P. 1437)

A **German trust company** has been organized for financing the purchase of **raw materials.** (P. 1473)

The **crude potash** situation in France is reviewed. (P. 1474)

Probably none of the wartime industries of Great Britain has shown greater development or more progress than that of **glass making.** (P. 1486)

The Balkan Peninsula is said to be a good region for the manufacture of **nitrates from the air** because of the abundant water power. (P. 1490)

A chemical company has been founded in Rumania to manufacture **chemicals** from **raw materials.** (P. 1490)

The total production of **whale oil** in Norway during 1919 was 23,654 metric tons, which is considerably less than the normal output. (P. 1505)

Foreign markets for **inks** are reviewed. (Pp. 1528–9)

The condition of the **French mines** and the **iron and steel industries** is reviewed. (Pp. 1588–91)

The **tin** supply of **South China** will soon go out of the markets of the world unless there is a rapid and complete change in the situation. Chinese tin is produced on the basis of a silver dollar whose exchange value is substantially that of $1 gold, while Straits Settlements tin, the chief competitor of Chinese tin in the markets of the world, is produced on the basis of a Straits dollar worth about 56 cents gold. (Pp. 1596–7)

The great scarcity of coal in France has caused some railway companies to transform their **motive power** from coal to fuel oil consumption. (P. 1597)

The **gutta-percha industry** is reviewed and statistics are given showing the quantities, values, and countries of destination of gutta-percha and gutta inferior exported from Singapore during 1918. (Pp. 1608–9)

For some years the production of **kauri gum** in New Zealand has been decreasing. (P. 1611)

It is anticipated that the production and exportation of **palm oil** on the east coast of Sumatra will continue to increase. Exporters have been handicapped by a lack of suitable containers. Some shipments made in locally constructed wooden barrels resulted in a loss through leakage of 30 per cent. (P. 1614)

Statistics showing the production of **copper** in Sweden are given. (P. 1615)

The **British dyestuffs industry** has made considerable progress during the past year, but there is still a scarcity of certain colors. It is hoped with the greater attention now being paid to research departments the results will be more satisfactory, and that England will secure a powerful place in the world's markets. (P. 1636)

An account is given of **foreign markets** for **soaps** and **soap-making materials**, including Algeria, Argentina, China, Jamaica, and Switzerland. (Pp. 1638–41)

A description is given of the **vegetable oil-bearing materials** and products in Spain. (Pp. 1646–54)

The **international metric system** of weights and measures is the only system authorized in **Belgium.** Although on account of the disturbed state of affairs in Belgium there has been laxity in the enforcement of the use of the metric system, the disposition is to have it obeyed. (P. 1654)

The **American purchase of certain Bolivian petroleum deposits** is announced and a railway line from Santa Cruz to Formosa is contemplated. This will serve as a very important gateway to a hitherto untouched section of Bolivia, the riches of which are known to be considerable. (P. 1656)

Statistics are given showing the production of **metals** in **Mexico** since 1916. (P. 1661)

Aluminum is being considered by the Japanese hydroelectric plants to **replace copper** in their heavy transmission cables. (P. 1662)

A **reward** of £10,000 is offered for the discovery in Australia of **petroleum** in commercial quantities. (P. 1670)

There is a demand for **heavy chemicals** in the Far East which should increase with the industrial development of that region. (P. 1705)

Considerable quantities of **sole leather** have been produced in China and beginning with 1920 the production of chrome leather of practically all ordinary grades was commenced. The quality of leather produced is of the cheaper grades and it is believed that there will be little clashing of interest between the American and European and the Chinese leathers. (P. 1708)

The prohibition on the importation of **dyestuffs** into British India has been removed. (P. 1729)

Artificial silk is being manufactured by the British Cellulose and Chemical Manufacturing Co. in Great Britain. The silk thread is of such texture and quality that when converted into articles of clothing it will have the appearance and finish of natural silk. When fully developed one factory alone will produce 9 tons of artificial silk a day. The company also manufactures noninflammable films, synthetic perfumes, and aspirin. (P. 1739)

An Australian manufacturer has invented and patented a new composition called **"Keltona,"** made partly from waste products, which can be used for imitation tiling, chair bottoms, and for most purposes for which thin woods and stones can be used. (P. 1756)

The exportation of **nitrate of soda** from Chile during January 1920 was the largest in any one month in the history of the nitrate trade. (P. 1763)

There is said to be a steady demand in Sweden for **drugs** from the **United States.** In the case of salvarsan there is a most serious opposition to be met on account of the distinct predilection among Swedish medical men to the use of the original German product. Among other drugs which could be advantageously introduced are senega root, golden seal, sabadilla seed, and barbital. (P. 1779)

A decrease in the **opium crop** in Greek Macedonia is reported in 1919. (P. 1788)

The **drug** and **chemical trade** of Japan is briefly reviewed. (P. 1799)

Special Supplements Issued

Scotland—22*a*
British West Indies—25*a*
Costa Rica—27*a*
Cuba—28*a*
Guatemala—32*a*
Salvador—39*a*
British India—53*c*
Egypt—71*a*
Madagascar—72*b*

Statistics of Exports to the United States

Hongkong, China—(pp. 1254–5)
Antimony
Camphor
Chemicals
Explosives
Fibers
Hides
Leathers and manufactures
Peanut oil
Wood oils
Aniseed oil
Cassia oil
Bismuth
Manganese
Wolfram
Paper and manufactures
Tin
Wood, unmanufactured and manufactured
Persia—(p. 1787)
Gum tragacanth
Opium
Skins, raw
France—(pp. 1305–9)
Aluminum
Chemicals
Hides and skins
India rubber scrap
Paper
Perfumery and soap
Potash
Rubber goods
Saffron
Belgium—(pp. 1403–4)
Horsehides
Rabbit skins
Glass
Calfskins
Anilin colors
Red powdered arsenic
Silver sand
Marble and flint stone
Crude rubber
Medicinal plants
Fusel oil
Muriate of potash

BOOK REVIEWS

Technical Handbook of Oils, Fats and Waxes. Vol. II—Practical and Analytical. By PERCIVAL J. FRYER, F.I.C., F.C.S., Chief Chemist and Director, Yalding Mfg. Co., Ltd., Lecturer in Oils, Fats and Waxes at the Polytechnic, Regent St., W. London Institute, and FRANK E. WESTON, B.Sc. (1st Hons.), F.I.C., Head of the Chemistry Dept., the Polytechnic, Regent St., W. xvi + 314 pp. 69 figures. Cambridge University Press, London, England, 1918. Price, $4.50.

The present volume considers the practical and analytical sides of oil and fat chemistry in the condensed and systematic manner characteristic of Volume I. The work is useful to the technical and industrial analyst, and perhaps even more so to the advanced college student of the subject. Practically all of the well-known methods for the testing and analysis of oils, fats, waxes, fatty acids, higher alcohols, glycerol, hydrocarbons and rosin and turpentine are given. It will be remembered that analytical methods were merely catalogued in the first volume. Excellent discrimination and judgment are shown in the selection of methods and all of the more important and some not so important are included. The illustrations are mainly from photographs, including apparatus of the fixed metallic and optical sort, and also assembled glass apparatus used in various tests. Diagrams and tables are frequent. The greatest drawback to the work is the lack of references to original literature for use in connection with various methods of analysis and tests, which tends to restrict the use of the book to beginners. Although a few such references are given, they are not general and numerous tests and methods are without references. The book is well printed on good paper. It will be found useful in all oil and fat libraries, particularly for quick reference.

W. D. RICHARDSON

Chemical Calculation Tables. By HORACE L. WELLS. 2nd Ed., Revised. John Wiley & Sons, Inc., New York. Price, $1.35.

In preparing the second edition of this volume, first issued in 1903, the author has taken the opportunity to revise the volume by recalculating the constants in accordance with what the author designates as the latest international table of atomic weights, leaving the reader to ascertain what particular table has been used. The recalculation of the constants seems to have been made with great care, the author realizing the importance of accuracy in tables of this kind.

The volume includes a rather brief table of Gravimetric Factors with a table of Formula-Weights, Factors for Indirect Analyses and a table for the Reduction of Gas Volumes, and also a table for Calculation of Nitrogen from the Gas Volumes. These tables do not cover at all completely the factors required by the analytical chemist.

The Gravimetric Factors in addition to the substance weighed include only metals and their oxides and occasionally carbonates or sulfates so that the analytical chemist would have to add a great many factors for his every-day use. The selection of the factors to be included is not always the best possible. For instance, under lead, the factors for converting PbS to Pb and PbO are given, while the factors for conversion from PbO_2 are not given. It is doubtful if lead is ever weighed as PbS, while in electrolytic work small quantities are frequently obtained as PbO_2 which would have been a much better factor to have included.

The table of Multiples for Organic Compounds will no doubt be found useful as well as the table for Molecular-Weight Determinations. The table for Weights and Measures is very limited.

The five-place table of Logarithms is undoubtedly the most valuable part of the volume as this table is very well printed and is extremely convenient for use, being very well thumb-indexed and very legible.

J. C. OLSEN

The Petroleum Handbook. By STEPHEN O. ANDROS, A.B., B.Sc., E.M. 206 pp. 48 illustrations, 17 tables. Shaw Publishing Co., 910 South Michigan Ave., Chicago, Ill. Price, $2.00.

This book, as stated by the author, is a compilation of general information on the origin, production, refining and marketing of petroleum and its products. It contains a chapter on Gasoline Specifications and State Laws covering gasoline and kerosene.

There is no new information contained in the book. The compiler has evidently made no attempt to discover and point out the errors in the original publications. The description of the methods of refining is very general and is incorrect in a great many cases. He states that the vacuum distillation process is in use in some refineries, whereas I know of no place where it is in use at the present time.

The compiler states that the method of refining asphalt base petroleum is substantially the same as in paraffin base, whereas, in fact, it is handled very differently.

On page 87 he states that the final boiling point of kerosene distillate is 450° F., whereas it is nearer 600° F.

The operation of the Trumble process (p. 95) is described in such a manner that one perfectly familiar with the process would not even recognize it.

The tabulation of the State Laws and Gasoline and Kerosene Specifications is also incorrect in a great many cases.

This book has the same objectionable features that I have noticed in others of this kind which have been recently published, in that although it is a useful compilation of information for one who had has experience in oil, it is a very poor guide for a beginner.

G. W. GRAY

Creative Chemistry. By EDWIN E. SLOSSON. 311 pp. Century Company, New York City, 1919. Price, $2.50 net.

The prominence given to science by war activities has so emphasized it in the minds of the public that there is to-day a greater demand for scientific discussions presented in a popular way than has ever been the case heretofore. There is real need for a popular presentation of the interesting problems in the field of chemistry, and "Creative Chemistry" does much toward fulfilling this need. It is well written and illustrated and the public is sure to find it very readable.

From the chemist's standpoint one might question the wisdom of giving prices (as on page 141) in view of the constantly changing conditions in the chemical industry. At times there is a crossing of subjects which in no way detracts from the readability of the volume but suggests the possibility of a somewhat better arrangement in another edition of the work. There are a few inaccuracies of small consequence that might be eliminated the next time. The author seems to have had the same difficulty in adhering to his text as do some of our best-known lecturers who find a discussion of things chemical leading them into by-paths suggested as the subject is developed. It would seem worth while to present such valuable diagrams as those presented on page 147 in more legible form and the addition of discussions at some points or the inclusion of a glossary would seem helpful.

The reading references are particularly valuable, especially to those who desire supplementary reading on various chemical subjects. The numerous bits of humor which Mr. Slosson has sprinkled through the text will be appreciated, and the book should have a wide appeal, doing much toward creating the scientific public of which the chemist is in need.

H. E. Howe

White Lead—Its Use in Paint. By A. H. Sabin. 128 pp. John Wiley & Sons, Inc., New York, 1920. Price, $1.25.

The purpose of this book is to give simple information regarding white pigments rather than to present the matter from the strictly chemical or scientific standpoint. It outlines briefly the history of the white lead industry, touching upon the methods used in the production of white lead by the Old Dutch, Carter, Matheson, mild, chamber, and various precipitation methods, and the process of sublimation. It describes briefly the methods used for drying, pulp mixing, and washing white lead, commenting upon the fineness, opacity, adhesion, water resistance, durability, methods of mixing, application, defects, etc. In the discussion of water resistance, affinity between lead and oil, etc., the author's statements are rather vague and not in agreement with present conceptions of physical chemistry.

Information is given regarding methods of mixing white lead, how the pigment affects light tints made with blue or green, and how the white lead may occasionally be discolored through effect of sulfur gases in certain industrial communities. The discussion on lead-poisoning is well presented, but the statements made on page 59 are contradictory.

Information regarding leaded zinc, lithopone, zinc oxide, and their use in modern flat and gloss paints is presented in an interesting but not impartial manner.

An outline of the proper method of reducing, thinning, and tinting white lead paste for application to various kinds of lumber ollows.

The volume should prove of value to the painter and to the student interested in paints.

H. A. Gardner

Mining and Manufacture of Fertilizing Materials and Their Relation to Soils. By Strauss L. Lloyd, E.M. vi + 153 pp.; illustrated. D. Van Nostrand Company, New York City, 1919. Price, $2.00.

The author expresses the hope that the book "will appeal not only to manure manufacturers, but to farmers, as well as to agricultural students and all those who take an intelligent interest in the subject of agricultural chemistry." The book is divided into fourteen chapters. It treats of the functions and sources of nitrogen, phosphoric acid and potash, the action of lime and gypsum, nitrification and denitrification, the origin and composition of soils, and the relation between soils and fertilizing materials. The author presents in much detail the subjects of pebble phosphate ore and hard rock phosphate ore dressing and milling. Chapters are devoted to the more common fertilizer ingredients containing nitrogen, potash and phosphoric acid, and to the manufacture of superphosphate, precipitated phosphate, ammoniated phosphates, and complete fertilizers. Considerable space is devoted to the occurrence, mining and purification of nitrate of soda, and to the fixation of nitrogen as calcium cyanamide and calcium nitrate. Much attention is given to the mining and purification of the German potash salts, and to the liberation of potash from feldspars by artificial means. The book closes with two chapters on the analysis of fertilizers and soils.

It will be noted that the book covers a rather unusual combination of subjects and is more suited to the general reader than to the student or analyst seeking special information. Most students will have neither the time nor desire to go into so much detail in regard to phosphate mining and fertilizer manufacture and the analyst will prefer a book which is not so restricted in its scope.

Greater care should have been taken in the preparation of the text. For example, the author after speaking of the formation of starch, says that "in some unknown way it becomes soluble," so that it can be transferred from one part of the plant to another. He states that available phosphate "appears to hasten the maturity of plant." It would seem that he could have said "it does" so.

In discussing the action of lime he asserts that its chief function "is to improve the mechanical condition of the soil;" whereas most authorities hold that its chief function is to counteract soil acidity and to break up or transform certain toxic substances which occur in such soils.

The author says that chemical analysis "does not attempt to ascertain and state in which form or forms the nitrogen is present in a fertilizer." He is evidently not aware that the forms of nitrogen are determined and published in some of the northern states. He adds that "compounds of ammonia are quite uncommon in commercial fertilizers," which is not borne out by the large amount of sulfate of ammonia used in mixed fertilizers.

The sweeping statement that "the mineral forms of nitrogen, such as nitrate of soda and sulfate of ammonia, both dissolve easily in water, hence they would soon wash into the subsoil and out of reach of the plants," certainly needs great qualification.

The writer makes the assertion that "before nitrogen in ammonium sulfate or organic substances can be taken up by plant life, it must be converted into nitrates." It is, nevertheless, well established that many plants may use nitrogen in one or both of those forms without change to nitrates. It is also asserted that "the nitrogen in organic substances is chiefly in an albuminoid form," no reference being made to other proteins and simpler organic compounds.

In speaking of common salt no mention is made of the fact that sodium may replace some potassium in connection with the growth of at least certain cultivated plants, only the indirect action of the salt being mentioned.

Silica in the form of grains of sand is referred to as "forming the bulk of most soils,"—a statement which may perhaps be excused in the case of a resident of Florida. Reference is made to the formation of carbonate of lime by "organic activity" in the shells of the "crustaceans," whereas a reference to the mollusca would have seemed more appropriate if a single reference were to be made. In one place gypsum is referred to as "an important fertilizing material," and elsewhere it is stated that it does not furnish "needed plant food."

One is rather amazed at the broad, unqualified statement that "there is no way to tell, without experiment, what food constituents a soil lacks."

It is asserted that sulfate of ammonia "should be used only when the soil has been lately limed," regardless of the fact that large areas of soil require no lime.

A strong odor in a fertilizer is said to be "an indication that organic matter is decomposing and nitrogen is being lost," which is a rather surprising statement from one supposed to be familiar with the strong odor of sludge acid.

Other parts of the book are relatively much better, showing greater care in preparation or greater familiarity with the subject. Many an agricultural student or general reader will find in the book much that will be new to him, and consequently interesting.

H. J. Wheeler

NEW PUBLICATIONS

By Clara M. Guppy, Librarian, Mellon Institute of Industrial Research, Pittsburgh

Acids, Alkalies and Salts. G. H. J. Adlam. 8vo 121 pp Price, 2s. 6d. Sir Isaac Pitman & Sons, New York.

Asbestos and the Asbestos Industry; the World's Most Wonderful Mineral, and Other Fireproof Materials. A L. Summers. 12mo. 107 pp. Price, $1.00. Sir Isaac Pitman & Sons, New York.

Chemical Molecule: La Molecule Chimique. R. Lespieau. 287 pp. Price, 3 fr. 50. F. Alcan, Paris.

Chemistry: A Class Book of Organic Chemistry. Vol. II. J. B. Cohen. 156 pp. Price, 4s. 6d. Macmillan & Co., Ltd , London.

Chemistry and Technology of the Diazo-Compounds. J. C. Cain. 2nd Ed 199 pp. Price, 12s 6d. E. Arnold, London.

Chemistry for Textile Students. Barker North and Norman Bland. 379 pp Price, 30s. University Press, Cambridge.

Chemistry: Service Chemistry; Being a Short Manual of Chemistry and Metallurgy and Their Application in the Naval and Military Services. V. B. Lewes and J. S. S. Brame. 5th Ed. 8vo. 576 pp. 21s. Edward Arnold, London.

Chemists' Manual of Nonferrous Alloys. J. R. Downie. 168 pp. Price, 10s. E. & F. N. Spon, London; Spon & Chamberlain, Ltd., New York.

Coal: Chemistry of Coal. J. B. Robinson. 96 pp. Price, 3s. 6d. Gurney and Jackson, London. .

Cordage and Cordage Hemp and Fibers. Thomas Woodhouse and P. Kilgour. 12mo. 113 pp. Price, $1.00. Sir Isaac Pitman & Sons, New York.

Dyes: Manufacture of Intermediate Products for Dyes. J. C. Cain. 2nd Ed. 273 pp. Price, 10s. Macmillan & Co., Ltd., London.

Galvanizing and Tinning. W. T Flanders. 8vo. 354 pp. Price, $4.00. U. P. C. Book Co., Inc., New York

Hendricks' Commercial Register of the United States for Buyers and Sellers, 1919–1920. 28th Annual Ed. 2703 pp. Price, $12.50. S. E. Hendricks Co., Inc., New York.

Ions, Electrons, and Ionizing Radiations. J. A. Crowther. 276 pp. Price, 12s. 6d E. Arnold, London.

Iron: An Outline of the Metallurgy of Iron and Steel. A. H. Sexton and J. S. Primrose. 2nd Ed. 8vo. 572 pp. Price, 15s. Scientific Publishing Co., Salford, England.

Limes and Cements: Their Nature, Manufacture and Use. An Elementary Treatise. E. A. Dancaster. 2nd Ed. revised and enlarged. 220 pp. 7s. 6d C. Lockwood & Son, London.

Lubricants: Memorandum on Solid Lubricants. T. C. Thomsen and L. Archbutt. 28 pp. H M. Stationery Office, London.

Metallurgy: Practical Metallurgy. Thomas Turner. 2nd Ed. 108 pp. Price, 3s. 6d. C. Griffin & Co., London.

Oil Analysis: A Short Handbook of Oil Analysis. A. H. Gill. 9th Ed. revised. 215 pp. Price. $2.50. J. B. Lippincott Co., Philadelphia.

Organic Chemistry: Laboratory Manual of Organic Chemistry. H. L. Fisher. 8vo. 331 pp. Price, $2.25. John Wiley & Sons, Inc., New York

Rarer Metals: Mineralogy of the Rarer Metals. E. Cahen and W. O. Wootton. 2nd Ed. revised. 246 pp. Price, 10s. 6d. C. Griffin & Co., London.

Reagent Chemicals: Standards and Tests for Reagent Chemicals. B. L. Murray. 8vo. 400 pp. Price, $2.00. D. Van Nostrand Co., New York

Silk Industry and Trade: A Study of the Economic Organization of the Export Trade of Kashmir and Indian Silks with Special Reference to the Utilization in the British and French Markets. R. C. Hawlley. 172 pp Price, 10s. 6d. P. S. King & Son, Ltd., London.

Textiles: Piece Goods Manual. A. E. Blanco. Price, $1.25. Statistical Dept. of the Inspectorate General of Chinese Maritime Customs, Shanghai. (Sold by G. D. Stechert & Co , New York.)

Zinc and Its Alloys. T. E. Lones. 8vo. 136 pp Price, $1.00. Sir Isaac Pitman & Sons, New York.

NEW JOURNAL

Discovery: A Monthly Popular Journal of Knowledge. Ed. by A. S. Russell, 8 Severn Road, Sheffield. Price, 7s. 6d. Published by Mr. John Murray, 50a Albemarle St., London, W. 1, England (Sold by W. Wesley & Son, 28 Essex St. Strand, London, W. C., England.)

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Sugar: Extraction and Production of Sugar from Different Vegetable Sources. A. R. Ling. *Chemical News*, Vol. 120 (1919), No. 3124, pp. 98–101.

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Water: Filtration and Softening of Water. G. G. Hepburn. *The Chemical Age* (London), Vol. 2 (1920), No. 37, pp. 226–227.

MARKET REPORT—APRIL, 1920

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

		Apr. 1	Apr. 15
Acid, Boric, cryst., bbls.	lb.	.16½	.16½
Hydrochloric, com'l, 22°	lb.	.02	.02
Hydriodic	oz.	.19	.19
Nitric, 42°	lb.	.08½	.08½
Phosphoric, 50% tech.	lb.	.25	.25
Sulfuric, C. P.	lb.	.08	.08
Chamber, 66°	ton	22.00	22.00
Oleum	ton	27.00	27.00
Alum, ammonia, lump	lb.	.04	.04
Aluminum Sulfate (iron-free)	lb.	.03	.03
Ammonium Carbonate, pwd.	lb.	.13½	.14½
Ammonium Chloride, gran.	lb.	.18	.18
Ammonia Water, carboys, 26°	lb.	.10	.10
Arsenic, white	lb.	.14	.14
Barium Chloride	ton	175.00	175.00
Nitrate	lb.	.11	.11
Barytes, white	ton	25.00	25.00
Bleaching Powd., 35%, Works,	100 lbs.	4.00	4.50
Borax, cryst., bbls.	lb.	.09½	.09½
Bromine, tech., bulk	lb.	.85	.85
Calcium Chloride, fused	ton	22.00	22.00
Chalk, precipitated	lb.	.05	.05
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	8.25	8.25
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.50	1.50
Iodine, resublimed	lb.	4.10	4.35
Lead Acetate, white crystals	lb.	.14	.14
Nitrate	lb.	.15	.15
Red American	100 lbs.	.10½	.10½
White American	100 lbs.	.09½	.09½
Lime Acetate	100 lbs.	3.00	3.25
Lithium Carbonate	lb.	1.50	1.50
Magnesium Carbonate, Tech.	lb.	.12	.12
Magnesite	ton	65.00	65.00
Mercury flask	75 lbs.	98.00	104.00
Phosphorus, yellow	lb.	.35	.35
Plaster of Paris	100 lbs.	1.50	1.50
Potassium Bichromate	lb.	.40	.40
Bromide	lb.	.90	.90
Carbonate, calc., 80–85%	lb.	.22	.22
Chlorate, cryst.	lb.	.15	.15
Cyanide, bulk, 98–99%	lb.	.30	.30
Hydroxide, 88–92%	lb.	.30	.30
Iodide, bulk	lb.	3.10	3.35
Nitrate	lb.	.14	.14
Permanganate, U. S. P.	lb.	.75	.75
Salt Cake	ton	18.00	25.00
Silver Nitrate	oz.	.80	.80
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	3.25	4.00
Caustic, 76%	100 lbs.	6.25	6.00
Sodium Acetate	lb.	.08½	.08½
Bicarbonate	100 lbs.	2.25	2.25
Bichromate	lb.	.30	.30
Chlorate	lb.	.10	.10
Cyanide	lb.	.27	.27
Fluoride technical	lb.	.16	.18
Hyposulfite	100 lbs.	3.60	3.60
Nitrate, 95%	100 lbs.	3.85	3.80
Silicate, 40°	lb.	.02	.02
Sulfide	lb.	.06½	.06½
Bisulfite, powdered	lb.	.06½	.06½
Strontium Nitrate	lb.	.25	.27
Sulfur flowers	100 lbs.	3.75	3.75
Crude	long ton	30.00	30.00
Talc, American, white	ton	20.00	20.00
Tin Bichloride	lb.	.21½	.21½
Oxide	lb.	.60	.60
Zinc Chloride, U. S. P.	lb	.50	.50
Oxide, bbls.	lb.	.22	.22

ORGANIC CHEMICALS

		Apr. 1	Apr. 15
Acetanilid	lb.	.65	.75
Acid, Acetic, 28 p. c.	100 lbs.	3.00	3.25
Glacial	lb.	.14	.16½
Acetylsalicylic	lb.	1.00	.95
Benzoic, U. S. P., ex-toluol	lb.	.85	.85
Carbolic, cryst., U. S. P., drs.	lb.	.15	.15
50- to 110-lb. tins	lb.	.21	.21
Acid (*Concluded*)			
Citric, crystals, bbls.	lb.	1.20	1.18
Oxalic, cryst., bbls.	lb.	.45	.50
Pyrogallic, resublimed	lb.	2.50	2.50
Salicylic, bulk, U. S. P.	lb.	.55	.55
Tartaric, crystals, U. S. P.	lb.	.78	.83
Trichloracetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.16	.20
Alcohol, denatured, 190 proof	gal.	1.01	1.01
Ethyl, 190 proof	gal.	7.50	8.00
Wood, Pure	gal	3.00	3.50
Amyl Acetate	gal.	4.00	4.00
Camphor, Jap. refined	lb.	2.50	2.25
Carbon Bisulfide	lb.	.06	.06
Tetrachloride	lb.	.11	.11
Chloroform, U. S. P.	lb.	.30	.35
Creosote, U. S. P.	lb.	.75	.75
Cresol, U. S. P.	lb.	.18	.18
Dextrine, corn	lb.	.06¼	.06¼
Imported Potato	lb.	.14	.14
Ether, U. S. P., conc., 100 lbs.	lb.	.19	.19
Formaldehyde	lb.	.57	.53
Glycerin, dynamite, drums	lb.	.22	.21½
Starch, corn	100 lbs.	5.25	5.25
Potato, Jap.	lb.	.06	.06
Rice	lb.	.25	.25
Sago	lb.	.05	.05

OILS, WAXES, ETC.

		Apr. 1	Apr. 15
Beeswax, pure, white	lb.	.65	.65
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	.18	.18
Ceresin, yellow	lb.	.14	.14
Corn Oil, crude	lb.	.18	.17½
Cottonseed Oil, crude, f. o. b. mill	lb.	.17¼	.15½
Menhaden Oil, crude (southern)	gal.	.95	.95
Neat's-foot Oil, 20°	gal.	2.25	2.25
Paraffin, 128–130 m. p., ref.	lb.	.11½	.11½
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs.	bbl.	18.55	19.75
Rosin Oil, first run	gal.	.90	.90
Shellac, T. N.	lb.	1.35	1.35
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.95	1.95
Stearic Acid, double-pressed	lb.	.27½	.27½
Tallow Oil, acidless	gal.	1.70	1.60
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	2.35	nominal

METALS

		Apr. 1	Apr. 15
Aluminum, No. 1, ingots	lb.	.31½	.31½
Antimony, ordinary	100 lbs.	11.75	11.75
Bismuth	lb.	2.52	2.52
Copper, electrolytic	lb.	.18½	.19
Lake	lb.	.18¾	.19
Lead, N. Y.	lb.	.09¼	.09¼
Nickel, electrolytic	lb.	.45	.45
Platinum, refined, soft	oz.	155.00	155.00
Quicksilver, flask	75 lbs ea.	98.00	104.00
Silver	oz.	1.35	1.27
Tin	lb.	.61¼	.62¼
Tungsten Wolframite	per unit	7.00	7.00
Zinc, N. Y.	100 lbs.	9.00	9.00

FERTILIZER MATERIALS

		Apr. 1	Apr. 15
Ammonium Sulfate	100 lbs.	7.10	7.10
Blood, dried f. o. b. N. Y.	unit	8.00	8.00
Bone, 3 and 50, ground, raw	ton	48.00	48.00
Calcium Cyanamide, unit of Ammonia		4.00	4.00
Fish Scrap, domestic, dried, f. o. b. works	unit	7.25	7.25
Phosphate Rock, f. o. b. mine:			
Florida pebble, 68%	ton	6.85	6.85
Tennessee, 78–80%	ton	11.00	11.00
Potassium muriate, 80%	unit	2.60	2.60
Pyrites, furnace size, imported	unit	.18	.18
Tankage, high-grade, f. o. b. Chicago	unit	7.75	7.75

COAL-TAR CHEMICALS

Crudes

		Apr. 1	Apr. 15
Benzol, C. P.	gal.	.33	.33
Cresol, U. S. P.	lb.	.18	.18
Naphthalene, flake	lb.	.10	.12½
Phenol, drums	lb.	.15	.15
Toluol, 90%	gal.	.34	.34
Xylol, water white	gal.	.40	.40

Intermediates

		Apr. 1	Apr. 15
Acids:			
Anthranilic	lb.	2.75	2.75
Benzoic	lb.	.85	.85
Broenner's	lb.	1.75	1.75
Cleves	lb.	2.00	2.00
Cresylic, 97–99%	gal.	1.00	1.10
F	lb.	3.00	3.00
Gamma	lb.	2.50	2.50
H	lb.	1.85	1.85
Metanilic	lb.	1.70	1.70
Monosulfonic F	lb.	3.00	3 00
Napthionic crude	lb.	.70	.70
Neville & Winther's	lb.	1.90	1.90
Phthalic	lb	.60	.60
Picric	lb.	.25	.25
Sulfanilic	lb.	.35	.35
Tobias	lb.	2.25	2.25
Amido Azo Benzol	lb.	1.15	1.15
Aniline Oil	lb.	.35	.36
For Red	lb.	.65	.65
Aniline Salt	lb.	.47	.47
Anthracene, 80–85%	lb.	.75	.75
Anthraquinone	lb.	4.50	4.50
Benzaldehyde, tech	lb.	.75	.75
U. S. P.	lb.	1.25	1.10
Benzidine Base	lb.	1.40	1.40
Benzidine Sulfate	lb.	1.15	1.15
Diamidophenol	lb.	6.00	6.00
Dianisidine	lb.	9.00	9.00
p-Dichlorbenzol	lb.	.10	.10
Diethylaniline	lb.	1.40	1.40
Dimethylaniline	lb.	2.00	1.45
Dinitrobenzol	lb.	.36	.36
Dinitrotoluol	lb.	.43	.43
Diphenylamine	lb.	.85	.80
G Salt	lb.	.75	.90
Hydroquinone	lb.	2.00	2.00
Metol	lb	11.50	11.50
Monochlorbenzol	lb.	.12	.12
Monoethylaniline	lb.	2.15	2.15
a-Naphthylamine	lb.	.45	.45
b-Naphthylamine	lb.	1.15	1.15
b-Naphthol, crude	lb.	.65	.70
m-Nitraniline	lb.	1.00	1.00
p-Nitraniline	lb.	1.50	1.55
Nitrobenzol, crude	lb.	.16	.16
Rectified (Oil Myrbane)	lb.	.18	.18
p-Nitrophenol	lb.	.80	.80
p-Nitrosodimethylaniline	lb.	1.90	1.90
o-Nitrotoluol	lb.	.22	.22
p-Nitrotoluol	lb.	1.15	1.15
m-Phenylenediamine	lb.	1.35	1.35
p-Phenylenediamine	lb.	2.50	2.50
Phthalic Anhydride	lb.	.45	.45
Primuline Base	lb.	3.00	3.00
R Salt	lb.	.75	.75
Resorcin, tech	lb.	4.00	4.00
U. S. P.	lb.	6.00	6.00
Schaeffer Salt	lb.	.75	.75
Sodium Naphthionate	lb.	1.10	1.10
Thiocarbanilid	lb.	.60	.60
Tolidine, Base	lb.	1.75	1.65
Toluidine, mixed	lb.	.44	.44
o-Toluidine	lb.	.30	.30
m-Toluylenediamine	lb.	1.35	1.35
p-Toluidine	lb.	1.75	1.75
Xylidene, crude	lb.	.40	.40

COAL-TAR COLORS

Acid Colors

		Apr. 1	Apr. 15
Black	lb.	1.15	1.15
Blue	lb.	3.00	3.00

Acid Colors (*Continued*)

		Apr. 1	Apr. 15
Fuchsin	lb.	2.50	2.50
Orange III	lb.	1.00	1.00
Red	lb.	1.10	1.10
Violet 10B	lb.	6.50	6.50
Alkali Blue, domestic	lb.	4.75	4.75
Imported	lb.	8.00	8.00
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	2.00	2.00
Erythrosine	lb.	12.00	12.00
Indigotine, conc	lb.	3.00	3.00
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.50	1.50
Ponceau	lb.	1.00	1.00
Scarlet 2R	lb.	1.00	1.00

Direct Colors

		Apr. 1	Apr. 15
Black	lb.	1.00	1.00
Blue 2B	lb.	.70	.70
Brown R	lb.	1.80	1.80
Fast Red	lb.	3.50	3.50
Yellow	lb.	2.00	2.00
Violet, con't	lb.	2.20	2.20
Chrysophenine, domestic	lb.	2.25	2.25
Imported	lb.	3.80	3.80
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00

Oil Colors

		Apr. 1	Apr. 15
Black	lb.	.70	.70
Blue	lb.	1.65	1.65
Orange	lb.	1.40	1.40
Red III	lb.	1.65	1.65
Scarlet	lb.	1.75	1.75
Yellow	lb.	1.70	1.70
Nigrosine Oil, solution	lb.	.90	.90

Sulfur Colors

		Apr. 1	Apr. 15
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.90	.90

Chrome Colors

		Apr. 1	Apr. 15
Alizarin Blue, bright	lb.	7.75	7.75
Alizarin Red, 20% Paste	lb.	1.10	1.10
Alizarin Yellow G	lb.	1.00	1.00
Chrome Black, domestic	lb.	1.25	1.25
Imported	lb.	2.20	2.20
Chrome Blue	lb.	2.50	2.50
Chrome Green, domestic	lb.	1.50	1.50
Chrome Red	lb.	2.00	2.00
Gallocyanine	lb.	3.25	3.25

Basic Colors

		Apr. 1	Apr. 15
Auramine, O, domestic	lb.	2.50	2.50
Auramine, OO,	lb.	4.15	4.15
Bismarck Brown Y	lb.	.90	.90
Bismarck Brown R	lb.	1.20	1.20
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	6.00	6.00
Indigo, 20 p. c. paste	lb.	.85	.85
Fuchsine Crystals, domestic	lb.	5.00	5.50
Imported	lb.	12.00	12.00
Magenta Acid, domestic	lb.	4.25	4.25
Malachite Green, crystals	lb.	3.75	3.75
Methylene Blue, tech	lb	2.50	2.75
Methyl Violet 3 B	lb.	2.60	2.60
Nigrosine, spts. sol	lb.	.85	.85
Water sol., blue	lb.	.65	.65
Jet	lb	.90	.90
Phosphine G., domestic	lb.	7.00	7.00
Rhodamine B ex-con't	lb.	35.00	35.00
Victoria Blue, base, domestic	lb	6.00	6.00
Victoria Green	lb	6.00	6.00
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00

THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY

PUBLISHED MONTHLY BY THE AMERICAN CHEMICAL SOCIETY
AT ESCHENBACH PRINTING COMPANY, EASTON, PA.

Volume 12 JUNE 1, 1920 No. 6

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Subscription to non-members, $6.00; single copy, 60 cents, to members, 50 cents. Foreign postage, 75 cents, Canada, Cuba and Mexico excepted
Entered as Second-class Matter December 19, 1908, at the Post Office at Easton, Pa., under the Act of March 3, 1879
Acceptance for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized July 13, 1918.
Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Secretary, 1709 G Street, N. W., Washington, D. C.

EDITORIALS

HELP WANTED

The title of this editorial has a familiar sound in these servantless days, but our plea is different from those found in Sunday edition columns. We have been watching two things closely—the continuous gain in numbers of papers received from research laboratories, and the constantly increasing cost of paper. While these factors continue to rise, the printing appropriation remains constant.

We are doing our best to catch up with publications, so that papers may appear in print within reasonable time. All reviewers are being asked to indicate specifically how papers may be condensed without sacrificing the merits of the contributions. This is an awful burden to put upon the reviewers. The right place to put that condensation tax is, in the language of the income tax, at the source, and we appeal to authors to contract their articles in every way possible. Eliminate unessential matter, combine tables, use graphs, resort to every possible device to tell the story clearly but briefly—otherwise this office will disappear under a flood of manuscript. We don't want to disappear. Give us your help.

FROM THE SENATE GALLERY

On Tuesday, May 11, 1920, the Longworth bill was displaced from its position as the "unfinished business" of the Senate and returned to its regular place on the calendar. The press announced forthwith that the dye bill was dead. With this pronouncement we take the sharpest possible issue. Delayed in passage—yes, but dead—no. Time and again we have expressed the conviction that the Senate will pass the dye bill, safeguarding the American industry. That conviction is to-day as strong as ever, for it is based upon our confidence in the common sense, the intelligence and the patriotism of the members of the United States Senate.

In the early part of 1917 a determined filibuster by a small group prevented the Senate from granting the President the right to arm our merchant ships, but the will of the Senate to guard American rights against German aggression finally found the means of asserting itself. Now again a small group of senators has used the rules of the Senate to prevent action upon a measure which, while economic upon its face, is closely bound up with the whole question of preparedness of the nation for any future war that may arise. Statements to us from leading members of the Senate, Republicans and Democrats alike, are to the effect that a large majority of the Senate favors the bill. A subcommittee frankly opposed at the outset to the principles of the bill has unanimously espoused it. The full Finance Committee with one exception, Senator Thomas of Colorado, has given its approval. Before the Senate adjourns the will of the majority will assert itself—that is our prediction.

The details of that week of filibustering are given in our Washington correspondent's letter in this issue. It was our good fortune to sit in the Senate gallery the first two days, and we have now been able to read the full account of the proceedings in the *Congressional Record*.

Unfortunately the sudden calling up of the bill made it impossible for us to hear the splendid opening speech of Senator Frelinghuysen of New Jersey on Saturday afternoon, May 1. Nor could we hear the able address in behalf of the bill by Senator Nugent of Idaho on Saturday, May 8. We did, however, hear many of Senator Nugent's pointed questions addressed to Senator Thomas. These showed what a clear grasp of the subject he had obtained when it was presented before the subcommittee.

From the gallery it was a very lonesome scene on the floor of the Senate Monday afternoon. Senator Thomas was speaking, evidently prepared for a long siege. Four or five senators, known to be opposed to the bill, sat in at the speech, and on the back row sat Senator Nugent, always on guard, missing no point. Clearly a filibuster was on. The smile of satisfaction on Senator Thomas' face during one of the quorum roll calls showed clearly that he was well satisfied with his efforts. Senators Kenyon of Iowa and Moses of New Hampshire were in frequent conference.

Speaking of Senator Moses, geography is a strange thing. Whoever would have thought that the opposition to this bill would have brought about so close a union of two towns, Manchester, N. H., and Sunbury, Pa.! Naturally one thinks of Manchester and the great Amoskeag Manufacturing Company when one thinks of Senator Moses. But what about Sunbury, a small Pennsylvania town of 15,000 inhabitants, according to the census of 1910? Doubtless it has grown some since then. Our attention was first called to Sunbury by the Report of the Alien Property Custodian which shows (pages 133 and 352) that the Custodian seized 80 per cent of the stock (preferred) of the Susquehanna Silk Mills, Sunbury, Pa., because it was enemy-owned. At Sunbury are located also the Sunbury Converting Works, which we are informed were owned by the Susquehanna Silk Mills. At the Senate hearings a rather violent attack upon the bill was made in the form of a statement filed by the Sunbury Converting Works. Furthermore, among the signers of the rather notorious "Memorandum in opposition to the purchase by the Government through the Textile Alliance, or other official agency, of dyes directly from the foreign manufacturers" appeared again the name of the Sunbury Converting Works. Now it appears that both the Susquehanna Silk Mills and the Sunbury Converting Works were represented legally by Mr. Harry S. Knight, of Sunbury, Pa., at the time of the seizure by the Alien Property Custodian. But we are getting ahead of the story, for we learned that only to-day. To resume—after the bill had received the approval of the Committee, Senator Moses introduced an extensive amendment, which dye manufacturers immediately felt could have no other effect than the destruction of the American dye industry. Fortunately the Tariff Commission studied the amendment and reported to the Finance Committee that it was unworkable. But that isn't the interesting part of the story. In April an extensive reply to the criticism of the Tariff Commission was made by Mr. Harry S. Knight, of Sunbury, Pa. His reply showed such an intimate acquaintance with the Moses amendment that one could easily get the impression that he had written the amendment himself. On our journey to Paris last fall we had a delightful ship-companion in the person of Mr. Harry S. Knight, of Sunbury, Pa. At that time we knew nothing of his interest in dyes. On Tuesday afternoon, we entered the Senate gallery and were surprised to find in the same section our ship-companion, Mr. Knight,—surprised, because we had not associated him for a moment with the Mr. Knight who had replied to the Tariff Commission's criticism. Toward the end of the afternoon Senator Moses left the floor, seemingly somewhat hurried. While leaving he passed near our gallery and motioned toward that part of the gallery where Mr. Knight was sitting. Immediately Mr. Knight rose and the two left the Chamber by different doors but at the same moment. Perhaps it was a mere coincidence. Possibly Mr. Knight had a sudden uncontrollable desire to take a smoke. We know not. There are some who even go so far as to believe that Mr. Knight wrote the Moses amendment. Again we know not.

Senator Thomas evidently out-Keynes Keynes in his views on the necessity for early restoration of German industrial prosperity, even at the expense of our own industries. The Senator, judging by his remarks, has also no sympathy for legislation intended to protect and develop American industries. His two main arguments are peculiar and somewhat difficult to grasp clearly. In the first place he contends that Germany has no stocks, is prostrate economically, and cannot manufacture enough dyes even for its domestic needs; yet he complains of "the enormous burden which this bill, should it become a law, will inflict upon the consumers of America." If Germany is unable to supply dyes, what burden can the embargo feature place upon our consumers? His is the argument of the importers, and they are not wasting their breath on economic principles. They are out after business. The second argument of the Senator is based upon the prosperous showing of one American dye manufacturing company. Such prosperity he repeatedly states is due to the present tariff law. Doesn't the Senator realize that the present tariff law has had no protecting influence upon the American industry? Since the raising of the blockade of German ports the Trading-with-the-Enemy Act has protected the American industry. The Senate recognized the necessity of such protection when it passed the Penrose resolution last winter extending the powers of the War Trade Board in case peace was declared before action could be taken on the dye bill.

In support of his general position, Senator Thomas fills the *Record* with lengthy quotations from the testimony of the importers. Mr. Metz, Mr. Sykes, Mr. Pickhardt, Mr. Fortner, Mr. MacKinney, are all called upon to support his contention.

The Senator made a great ado about Dr. Hesse, whom he placed upon the highest pinnacle of dyestuff authorities, and about his address before the Franklin Institute on November 6, 1919. While admitting that Dr. Hesse advocated the license features of the House bill, nevertheless he, like Mr. John P. Wood during the hearings, insisted that this address of Dr. Hesse's constituted the most convincing argument against the bill, because Dr. Hesse contended that

> "we can surely have all of these other industries [explosives, photographic chemicals, synthetic medicinals, 'toxic and like gases for military purposes whose invention and development belong to the Chemical Warfare Service'] in the highest possible state of efficiency if we only will, whether we have a dye industry or not. That we should have our own supply of dyes is the only reason for having a domestic dye industry. The war itself proved that conclusively and beyond question."

When Senator Nugent inquired if it meant nothing to the Senator that the resolutions unanimously passed at the recent meeting of the AMERICAN CHEMICAL SOCIETY embodied views quite at variance with those of Dr. Hesse, Senator Thomas clung to his idol still.

The Senator bombarded Mr. Irenee du Pont because Mr. du Pont "asks for the suspension of the Sherman anti-trust law, not as affecting the whole country but only as affecting the dye industry." That is not what Mr. du Pont said, or rather it is only a part of what he said. Here are Mr. du Pont's words, as recorded in the official hearings of the subcommittee, page 166:

> I want further then and at the risk of seeming to get a monopoly, to urge that you should provide that the Sherman law does not apply to the dye industry, if it is thought necessary in the opinion of some Government official. I say that not because we want a monopoly; we do not want it; if we have everybody competing for the prizes, that is the ideal way. But suppose some unexpected situation happens, requiring that we get dye makers together on short notice to exchange information, some Government officer ought to be designated to say the Sherman Act does not apply to the dye industries, because it is in the interests of the public need, if that time ever comes.

That is a very different proposition from the one the Senator in his speech ascribed to Mr. du Pont, who clearly referred to the exigencies of war. We are confident every member of the subcommittee so understood it.

There's a whole lot more that could be said in comment on the Senator's speech, but our space reserved for editorials is limited and there is one personal point we wish to make clear. While admitting that he found himself "unable to turn to the citation," Senator Thomas claimed that we had stated "that the amount of dyestuffs in storage in Germany or under Germany's control amounted to something like 250,000 tons." Of course he couldn't find the citation. That is an old debater's trick. The citation doesn't exist. If the Senator or anyone else can find in our testimony the statement that we considered German stocks to be "something like 250,000 tons," we will agree never to appear before another congressional committee.

No, the opposition has so far prevented a vote: it has raised a smoke screen about the Levinstein agreement and about the Weston letter, which Senator Kenyon said General Wood resented, but about which General Wood is quoted in the New York *World* of May 9, 1920, as saying: "Of the letter published this morning I knew nothing until I saw it in the papers," but such matters cannot cloud the real issue.

Meanwhile the delay is hurting. The publication on May 10, 1920, by the New York *Journal of Commerce* of the 1920 monthly totals of capital authorized in the chemical, drug and dye industries is extremely suggestive:

January	$17,943,000
February	12,585,000
March	29,660,000
April	4,670,000

That April figure tells a story!

DR. MANNING RETIRES

To-day marks the retirement of Dr. Van H. Manning from the Directorship of the U. S. Bureau of Mines to assume his new position of Director of Research for the American Petroleum Institute.

Succeeding Dr. Joseph A. Holmes, the first Director of that Bureau, Dr. Manning has carried forward steadily and with constant initiative the work of the Bureau of Mines which has proved itself so potent a factor in the economic development of the natural resources of the country. He has infused the personnel of the Bureau with an *esprit de corps* which has greatly facilitated its usefulness and proved him a born organizer.

The chief obligation which the country owes him, however, is for the part he played in inaugurating the first developments of chemical warfare in this country. With clear prevision he joined heartily with the members of his staff in inaugurating the work of the American University Experiment Station. Bureaucratic methods were minimized and results, therefore, rapidly obtained. It is as the real founder of the Chemical Warfare Service that we shall always think of him, and he may rest assured that he carries with him into his new work the best of good wishes from all who were associated with him in this patriotic and timely service.

NOTES

New chemical laboratories continue to be provided at our universities. The latest good news is from the University of Mississippi. The Legislature has appropriated $350,000 for a new building for the departments of chemistry and pharmacy. Professor Swan's good work has made its impress.

The award of the Remington Honor Medal in Pharmacy to Dr. John Uri Lloyd, of Cincinnati, was an event which brought happiness to the many friends of that genial soul and indefatigable worker. His work will prove of enduring value to pharmacy, and his happiness over the medal award will be shared by his "children," who always "listen" when he raises his good right arm.

According to Consul Henry B. Hitchcock, of Taihoku, Taiwan, the Japan Camphor Monopoly Office has guaranteed a minimum allotment of camphor to the United States for the period of April, May, and June 1920, of 327,386 pounds, with the possible, though not probable, likelihood of permitting a maximum allotment to the United States of 349,000 pounds. The prices per hundred weight are given as 227 yen ($113.16) for grade B and 255 yen ($127.12) for grade BB.

Doubtless we ought to be grateful to the Camphor Monopoly for granting to America the privilege of securing this many pounds of grade B and that many pounds of grade BB, at prices which the Monopoly fixes. As a matter of fact we are not grateful; on the contrary, the statement riles us. Where is the spirit of American economic independence? Camphor can be made from spirits of turpentine, a crude material produced chiefly in this country. No one expects the present abnormally high price of turpentine to hold indefinitely. In a previous issue we urged the development here of synthetic camphor manufacture. That urging is repeated, and with even greater emphasis.

The printing ink manufacturers are plain-spoken men. They never straddle a question. One has only to know Phil Ruxton, their leader, to appreciate the accuracy of this characterization. It is therefore of particular significance that at their annual convention in New York City on May 11, 1920, the following resolution was unanimously adopted and promptly forwarded to members of the United States Senate:

> Resolved that it is the unanimous sense of this meeting that this association petition United States Senate to pass immediately coal-tar dye H. R. eight naught seven eight as reported by the sub-finance committee of the Senate.

In our address at the General Meeting in St. Louis appreciative attention was called to the liberal regulations of the U. S. Bureau of Internal Revenue for the administration of the special section of the National Prohibition Act which provides for the production, sale, and use of an ample supply of alcohol for industrial and scientific purposes. So far, so good. But there are indications of a fly in the ointment. Just at present it looks a little as though the Deputy Commissioners are so busy trying to enforce the prohibition side of the matter that not one of them has time to give especial attention to the administration of the chemical end of the question. Possibly we are overanxious. It is to be hoped that is the case.

Don't be misled if you see circulars stating that the Nolan bill has passed both the House and the Senate, has been signed by the President and is now law. The statement is true but is somewhat misleading. There are two Nolan bills, the one giving protection to trademarks, now a law; the other giving relief to the Patent Office organization and administration. The latter passed the House with only one dissenting vote. It is still before the Senate. Letters from individual chemists to their senators and to the chairman of the Patent Committee, Senator George W. Norris, might overcome this condition of stillness. Do it to-day!

THE CHEMICAL INDUSTRY AND TRADE OF ITALY

By O. P. Hopkins, Washington, D. C.

For many years Italy has exchanged her surplus agricultural products, such as wines, silk, and citrus fruits, for the manufactured goods she did not produce at home. Her own industries have been handicapped by the almost total lack of coal, iron, cotton, and other basic materials. The war demonstrated the weakness of her economic situation, and there has developed a determination to make the country as independent industrially as possible, in which direction conspicuous success has already been achieved in the manufacture of automobiles and cars for railroads and street railways.

In this effort toward greater industrial independence there are two favorable factors that tend to offset the lack of materials; that is, an abundance of good labor and great waterpower resources, although the shortage of materials can never really be made up within the present geographic boundaries.

Before the war German capital was a controlling factor in the economic life of the nation, with the natural result that German manufactured products, including chemicals, found a ready market in exchange for Italian products of the soil.

Formerly the imports of chemicals from Germany were valued at about $10,000,000, of which something like $4,000,000 represented purchases of dyes. England supplied approximately $7,000,000 worth of chemicals, which included large quantities of heavy chemicals, particularly copper sulfate for the agriculturists and alkalies for the soap, glass, and textile industries. France supplied over $4,000,000 worth of chemicals, dyes, and medicines, and the United States less than $1,000,000 worth. During the war increased dependence was placed upon American chemicals, but the future of this trade will obviously depend in large measure upon the success of the Germans in restoring conditions at home that will enable them to reënter the market with the old advantages.

Italy's own chemical industries were not an important factor in the industrial situation at the time the war broke out. She supplied more than half of the world's consumption of sulfur and exported a few products based upon her citrus-fruit industry, such as citrate, upon her wine industry, such as tartaric acid, and also a number of essential oils.

The development of the chemical industries during the war has been studied carefully by the official Italian Committee for the Chemical Industries, and the results have been published in the "Annuario per le Industrie Chimiche e Farmaceutiche" (Rome, 1919), which includes a special census of chemical industries taken in 1918. The following observations on the situation in the most important branches, with the tables of production, imports, and exports, are based almost entirely upon this publication.

PRODUCTION OF ACIDS

The Italian production of hydrochloric acid was estimated at 39,015,000 lbs. in 1914 and there has been no marked change in the industry since. The average monthly production of the acid had increased to 3,968,300 lbs. in 1918, but the latter figure includes 992,000 lbs. of acid manufactured as a by-product in the preparation of monochlorobenzene, which ceased with the end of the war. Only about 66,000 lbs. of the acid are produced synthetically.

The output of nitric acid increased from 3,362,000 lbs. a month in 1915 to 15,763,000 lbs. in 1918, with a productive capacity of 21,870,000 lbs. Of the 1918 monthly output, 9,259,400 lbs. were used in the manufacture of explosives.

The monthly production of sulfuric acid by the chamber process has been maintained at about 110,000,000 lbs., all of which in 1918 was used in the manufacture of superphosphates or in the production of concentrated acid, all of the concentration plants being of the Kessler type with Elianite pans. The production of acid by catalysis has increased from 3,114,000 to 17,637,000 lbs. a month. The domestic production of iron pyrites was 317,334 metric tons in 1913, but increased to 500,782 in 1917. Imports, which amounted to 40,512 tons in 1913, had disappeared by 1917, whereas exports increased from 23,307 tons in 1913 to 194,328 in 1918.

The characteristic Italian product, citric acid, was produced in increasing quantities during the war, the monthly output jumping from 165,300 to 330,700 lbs. per month. The output of crude calcium citrate increased from 14,741,500 lbs. in the fiscal year 1914 to 20,033,400 lbs. in 1918. The exports of this product reached the high mark of 16,047,000 lbs. in 1916, but declined to 8,235,800 lbs. in 1918, which is slightly below the total for 1913.

The production of lactic acid has increased from 49,600 to 57,300 lbs. per month. There are also produced small quantities of lactates of calcium, iron, and antimony, various lactophosphates, etc.

A decrease from 341,700 to 251,300 lbs. per month has occurred in the production of tartaric acid, but a new factory is expected to triple the output. Exports of this by-product of the wine industry fell off from 6,274,800 lbs. in 1913 to 4,345,300 lbs. in 1918. The monthly production of cream of tartar, mostly refined, has increased from 154,300 to 253,500 lbs. Exports of this article amounted to very little before 1913, but reached a total of 3,208,800 lbs. in 1915, and then fell off to 1,333,100 lbs. in 1918.

The Italians are now turning out synthetic tannic acid at the rate of 22,000 lbs. a month, while the manufacture of tanning extracts has increased from 1,874,000 lbs. a month before the war to 4,299,000 lbs. The imports of tanning extracts, chiefly quebracho, have risen from 13,375,000 lbs. in 1914 to 33,563,000 lbs. in 1918.

SODA AND POTASH

Before the war Italy depended entirely upon imported sodium carbonate and caustic soda, but recently there has been a considerable production of caustic soda by the electrolytic process, amounting to about 4,409,200 lbs. a month, and in addition there is a growing output of other caustic soda. The importation of caustic soda, however, amounted to 33,547,700 lbs. in 1918, or about the same as reported for 1914. The imports of carbonate of soda fell off from 105,854,000 lbs. in 1914 to 49,937,800 lbs. in 1918. Shipping conditions for the last few years have made it difficult to get the supplies needed. Bleaching powder has been produced in the usual quantities in connection with the soda industry.

The production of sodium acetate has declined from 44,000 to 22,000 lbs. a month, owing to the shortage of calcium acetate and acetic acid. The existing plants can produce 507,000 lbs. of acetate a month. The output of sodium bisulfite has been maintained at 352,700 lbs. a month, of which 132,300 lbs. were used in 1918 by the producing firms in further manufacture. The monthly output of sodium thiosulfate shows a rather striking increase from 44,000 to 220,460 lbs., and the capacity of the present plants is given as 352,700 lbs. An increase from 2,535,300 lbs. per month to 3,218.700 lbs. is recorded for sodium sulfate, about 1,102,300 lbs. of the amount for 1918 being retained by the producers for further manufacture. The output of Glauber's salt has increased from 1,697,600 to 1,984,160 lbs. per month. Imports of sodium sulfate amounted to 22,865,900 lbs. for the year 1913, reached a maximum of 48,777,500 lbs. in 1916, and declined to 16,236,600 lbs. in 1918. The production of sodium sulfide averaged 992,000 lbs. a month before the war during the working seasons, but fell off to 562,200 lbs. in 1918, owing to the fact that the plants (which have a capacity of 1,984,000 lbs.) were idle because the electric furnaces were working on other products. As a result of war demands the output of sodium chlorate increased from 35,300 lbs. per month in 1914 to 1,477,000 lbs. in 1918. The monthly output of sodium phosphate has increased from 110,200 to 137,800 lbs. a month.

Potassium nitrate, which was produced to the extent of 2,094,400 lbs. in 1914, was turned out at the rate of 771,600 lbs. a month in 1918. It is made from the residues from distilleries and from imported potash salts in connection with which mention should be made of chloride imported from Erythrea to the extent of 1 395,700 lbs. in 1918.

CALCIUM CARBIDE AND CYANAMIDE

During the war the factories manufacturing calcium carbide and cyanamide were under government control and their output became irregular, as they were required to furnish various other products, such as silicon, ferrosilicon, and calcium silicate. They suffered also from a shortage of electric power. The factories in operation produced about 8,598,000 lbs. of calcium carbide per month, of which, however, 4,759.700 lbs. were consumed in the producing plants themselves in the manufacture of other products. The monthly output of cyanamide averaged 3,968,300 lbs., of which 3,174,600 lbs. were marketed, the remainder being employed in the production of sulfate of ammonia. The existing plants have a capacity of 12,346,000 lbs. of cyanamide a month. Neither calcium carbide nor cyanamide has been imported in large quantities.

AMMONIUM SULFATE SITUATION

Agricultural demands for ammonium sulfate have always been heavy in Italy, and previous to the war these demands were met pretty largely by imports. The care taken during the war, however, in collecting ammonia at the gas and coke plants for use in manufacturing war supplies, has resulted incidentally in an increased output of ammonium sulfate. The monthly output before the war was about 2,535,000 lbs., whereas in 1918 it was about 7,275,000 lbs., of which 5,622,000 lbs. were produced in gas works, 880,000 in coking plants, 660,000 in cyanamide plants, and 113,000 in plants distilling peat. In the meantime imports have fallen off from 48,000,000 lbs. in 1913 to 5,500,000 lbs. in 1918. When normal conditions have been restored it is likely that imports will show an increase as compared with 1918, but it is also likely that the Italians will never be so dependent on foreign sources as they were before the war.

SHORTAGE OF PHOSPHATE FERTILIZER

As enormous quantities of sulfuric acid were needed for war purposes there was a marked reduction in the domestic output of superphosphates, and consequent injury to crops. This reduction was intensified by a decreased importation of natural phosphates and by the closing in November 1917 of a number of establishments in Venetia. The monthly production of superphosphate and various phosphatic fertilizers decreased from 170,300,000 lbs. before the war to 89,177,000 lbs. in 1918. Imports of phosphate rock decreased from 529,776 metric tons in 1913 to 231,679 tons in 1918. The net imports of chemical fertilizers amounted to 52,723 tons in 1913, but were negligible in 1917 and 1918. Agriculture suffered also from a shortage of Thomas slag, of which 119,257 tons had been imported in 1913. The production of bone phosphate decreased from 1,014,000 to 683,000 lbs. a month.

PRODUCTION OF COPPER SULFATE

The vineyards of Italy require liberal applications of copper sulfate and sufficient progress has been made in the manufacture of this poison during the war to warrant the belief that little will be needed from the outside in the future. Production was estimated at 69,010,000 lbs. for the year 1914, but the monthly output is now from 14,300,000 to 18,500,000 lbs., and the existing plants are said to have a capacity of 25,574,000 lbs. monthly. Imports totaled 48,280,400 lbs. in 1914, but in 1918 only 50,486 lbs. were purchased abroad.

COAL-TAR PRODUCTS

The scarcity of coal during the war seriously affected the production of gas and coke and was a serious drawback to the efforts to build up a coal-tar industry. The monthly production of tar in the gas works was 6,325,000 lbs. and at the coke ovens 2,756,000 lbs., in 1918. The plants for the distillation of tar have a capacity of 13,670,000 lbs. a month, but in 1918 the quantity distilled was 7,055,000 lbs., only a slight increase over the amount handled in 1914. The output of light tar oils was 88,200 lbs. a month in 1918, of medium oils 374,800 lbs., and of heavy oils and anthracene 727,500 lbs., each practically the same as in 1914. These products were turned out under the orders of the military authorities and were used in the manufacture of other war materials, and large quantities of light oils were imported for this purpose.

Prior to the war neither aniline nor its derivatives were produced in Italy, and the present production is limited almost exclusively to aniline salt, *p*-nitraniline, and aniline oil, and these are produced only in small quantities. The production of dyes was negligible before the war, amounting to not more than 8,800 lbs. a month. In 1918 the monthly output was 363,760 lbs., of which the bulk was sulfur dyes. The committee which prepared the report upon which this article is largely based calls attention to a number of new dyes that are now being made, but the total is unquestionably small, and, considering all the circumstances, it is quite likely that the day is not far distant when more or less complete reliance will again be placed upon imported artificial colors.

MINERAL COLORS

The output of mineral colors has greatly increased, rising from 1,345,000 lbs. per month in 1914 to 3,329,000 lbs. in 1918. Included in this total are cinnabar, white lead, minium and litharge, zinc white, chrome yellow and chrome green, English red, lithopone, and ultramarine blue. There has also been a small production of natural coloring earths. Of some importance, too, has been the production of blanc fixe, a by-product of the manufacture of hydrogen peroxide from the peroxide of barium. There has been a noteworthy production of the various salts of barium, particularly the carbonate, chloride, nitrate, and sulfate, as well as the oxide, hydrate, and sulfide.

SOAP INDUSTRY

The soap industry was hampered during the war by the scarcity of fats, so that more soap was imported than usual, although Italy has always depended rather heavily upon outside supplies. The production of soap in 847 factories in the fiscal year 1918 aggregated 252,780,000 lbs. The special census of 1918 was confined to 125 of the larger factories producing 10,692,000 lbs. a month, as against 11,905,000 lbs. before the war. In 1918 the imports of common soap were 18,921,000 lbs., or more than double the purchases in 1914, while the imports of perfumed soaps were 3,397,000 lbs. in 1918, as against only 384,500 lbs. in 1914. On the other hand, exports, which amounted to 8,011,000 lbs. in 1914, fell off to 870,000 lbs. in 1918. The production of glycerol and its use in explosives were highly developed during the war, and the requirement that no fats be used unless freed from glycerol increased the production of fatty acids. There were large imports of glycerol to meet war demands.

STATISTICS OF PRODUCTION

The following table shows statistically the development of the Italian chemical industry during the war and has been compiled entirely from the report of the Committee for the Chemical Industries. The special census taken in 1918 by this committee was based upon statements by the producers, which, it is stated, were in many cases verified by the committee's own representatives. As conditions were unsettled and production irregular, figures of average production for the working period were collected, so that in many cases it will not be correct to multiply such figures by 12 in order to obtain the annual output.

Production of Chemicals and Allied Products

	Average Monthly Production		Maximum Productive Capacity per Month
	1914–15 Lbs.	1918 Lbs.	1918 Lbs.
Chemicals:			
Acetate of aluminum	15,400	4,400	11,000
Acetate of calcium	121,250	114,600	297,600
Acetate of lead	75,000	158,700	165,300
Acetone	49,600	83,800	385,800
Acids (except carbolic):			
Acetic	44,000	49,600	132,300
Boric, crude	485,000	440,000	440,000
Refined	198,400	220,500	220,500
Carbonic anhydride	639,300	500,450	727,500
Citric	165,300	330,700	440,000
Hydrofluoric	.....	19,800	24,250
Hydrochloric	3,306,900	3,968,300	8,046,900
Lactic	49,600	57,300	115,700
Nitric	3,362,000	15,763,000	21,870,000
Oleic (olein)	2,491,200	1,183,900	3,108,500
Stearic (stearin)	1,951,000	683,400	2,171,500
Sulfuric, 50–52° Baumé	115,345,800	103,771,600	145,946,000
66° Baumé	6,172,900	32,077,200	35,714,900
Oleum	3,114,000	17,637,000	20,679,000
Sulfurous anhydride	4,410	26,450	72,750
Tannic	.....	22,000	22,000
Tartaric	341,700	251,300	771,600
Various fatty acids	628,300	1,146,400	1,763,700
Alcohol, methyl	14,330	24,250	74,950
Alum, chrome	.....	176,400	176,400
Aluminum oxide	324,100	606,300	661,400
Sulfate	595,200	346,100	1,455,000
Ammonia, reckoned as 100% NH_3	4,410	50,700	93,700
Ammoniacal liquor, concentrated	.....	4,075,000	.....
Ammonium:			
Carbonate	30,860	35,270	72,750
Chloride	13,200	.....	55,100
Nitrate	.....	1,444,000	2,006,200
Persulfate	.....	3,300	3,300
Sulfate	2,535,300	7,275,200	.....
Barium:			
Carbonate	.....	44,100	220,460
Chloride	110,200	154,300	220,460
Hydrate	330,660	49,600	330,660
Nitrate	1,100	93,700	99,200
Oxide	661,400	66,140	661,400
Sulfate	209,400	275,600	407,850
Sulfide	242,500	255,700	948,000
Caffaro paste (copper chloride in solution)	286,600	396,800	396,800
Calcium:			
Carbide	12,643,500	8,598,000	22,817,800
Carbonate	44,100	110,200	154,300
Hypochlorite	1,763,700	1,653,500	2,425,000
Carbon:			
Bisulfide	407,850	716,500	804,700
Oxychloride (phosgene)	.....	214,950	529,100
Tetrachloride	22,000	163,100	418,900
Chloral hydrate	.....	132	265
Chlorine, liquid	33,000	165,300	429,900
Citrate of calcium	(20,033,400 lbs. produced in 1917–18)		
Citrate of iron	440	3,300	4,400
Copper:			
Oxide	.....	6,600	6,600
Sulfate	14,330,000	18,518,800	25,573,600
Ether, sulfuric	123,500	694,500	1,488,100
Ferrocyanides of calcium, potassium, and sodium	27,560	17,630	49,600
Formaldehyde	16,500	.....	29,760
Glycerol	489,400	330,700	705,500
Hydrogen, compressed, in flasks, cu. ft	1,253,700	7,945,700	13,419,500
Hydrogen peroxide, 3 per cent	229,300	235,900	617,300
Iron:			
Oxide	38,580	44,100	149,900
Sulfate	396,800	388,000	573,200
Lactarine (casein)	9,920	18,700	22,000
Derivatives	6,600	11,000	17,600
Lactates	1,100	2,200	28,660
Magnesium:			
Carbonate	30,900	202,800	297,600
Chloride	6,600	44,100	82,670
Sulfate	191,800	275,600	992,000

PRODUCTION OF CHEMICALS AND ALLIED PRODUCTS (*Concluded*)

	AVERAGE MONTHLY PRODUCTION 1914–15 Lbs.	1918 Lbs.	MAXIMUM PRODUCTIVE CAPACITY PER MONTH 1918 Lbs.
CHEMICALS (*Concluded*):			
Mercuric chloride	9,920	3,300	22,000
Milk sugar (lactose)	99,200	19,800	125,700
Nitrogen, cu. ft	31,800	6,180[1]	233,000
Oxygen, cu. ft	4,237,700	11,018,100	17,127,500
Phosphorus	.....	110,230	176,360
Potassium:			
Aluminum sulfate (alum)	264,550	440,900	661,400
Bichromate of potassium and sodium	176,400	154,300	275,600
Bisulfite	.....	7,700	44,000
Chlorate	132,300	88,200	176,400
Nitrate	396,800	771,600	1,433,000
Tartrate, acid	154,300	253,500	463,000
Silver nitrate	2,425	1,540	7,716
Sodium:			
Acetate	44,000	22,000	507,000
Bisulfite	352,700	352,700	771,600
Borate (borax)	154,300	.....	154,300
Carbonate	.....	.....	2,645,500
Chlorate	35,300	1,477,000	1,587,300
Hydroxide (caustic soda):			
Fused	595,200	2,535,300	4,629,700
Solution	1,455,000	5,202,900	5,511,500
Hypochlorite	606,300	551,150	925,900
Peroxide	.....	6,600	22,000
Phosphate	110,200	137,800	242,500
Pyrophosphate	.....	5,500	33,000
Silicate	66,100	110,200	297,600
Sulfate:			
Anhydrous	2,535,300	3,218,700	4,100,600
Crystals (Glauber's salt)	1,697,600	1,984,160	3,439,200
Sulfide	992,080	562,200	1,984,160
Sulfite	4,400	66,100	77,160
Thiosulfate	44,000	220,460	352,700
Sulfur chloride	132,300	209,400	242,500
Thorium nitrate	.....	1,984	4,400
Tin:			
Chloride	66,100	66,100	220,460
Oxide	.....	2,200	22,000
Zinc:			
Chloride	.....	138,900	275,600
Sulfate	4,400	4,400	37,500
COAL-TAR PRODUCTS:			
Aniline and its derivatives	.....	242,500	584,200
Anthracene, crude	29,760	84,880	123,460
Benzene:			
Crude	.....	843,270	1,069,240
Rectified	19,840	790,160	925,900
Carbolic acid:			
Crude phenol	11,000	55,100	99,200
Refined phenol	.....	899,500	1,212,500
Coal tar	.....	9,125,900	.....
Coal-tar dyes:			
Sulfur dyes	4,400	335,100	1,005,300
Other	4,400	28,660	1,287,500
Naphthalene, sublimated	63,900	134,500	209,400
Naphthol, beta	.....	7,500	33,000
Tar oils:			
Heavy	712,500	727,500	.....
Light	103,600	88,200	.....
Medium	368,200	374,800	.....
Toluene	.....	242,500	330,700
Xylenes	.....	40,800	63,300
OTHER PRODUCTS:			
Albumin	5,070	3,968	6,834
Asparagin	22	.....	44
Fertilizers:			
Bone phosphates	1,014,100	683,400	1,058,200
Calcium cyanamide	4,585,600	3,968,300	12,345,900
Superphosphates	170,307,000	89,177,000	225,092,000
Glucose	1,609,400	1,499,100	2,502,200
Glue:			
Common	870,800	749,600	1,322,800
Casein glue	.....	32,000	66,100
Shoemakers' glue	4,400	.....	99,200
Greases:			
Bone fat	374,800	297,600	661,400
Lanolin	.....	1,320	2,640
Gums and resins:			
Dextrine	551,150	187,400	1,267,700
Rosin	66,100	44,000	176,400
Malt extract	176,400	52,900	253,500
Mannitol	4,400	5,510	11,000
Oils:			
Fixed: seed oils	4,960,400	4,739,900	7,936,600
Refined	.....	44,000	88,000
Resin oil	33,000	22,000	110,000
Volatile: essences of citrus fruits	(2,248,700 lbs. produced in 1917–18)		
Paints, pigments, colors:			
Minium and litharge	388,000	1,845,300	2,050,300
Ultramarine	.....	28,660	81,570
White lead	507,000	683,400	112,400
Zinc white	346,100	545,600	882,000
Other mineral colors	103,600	226,000	491,600
Soap	11,905,000	10,692,400	23,479,200
Tar, vegetable	55,100	110,200	308,600
Turpentine, spirits	13,200	11,000	35,300
Wood pulp	220,500	1,433,000	2,645,500

[1] Compressed.

IMPORT STATISTICS

The fact that Italy was largely dependent upon imported chemicals before the war is amply demonstrated by the following table, which also shows the effect of the war on this import trade. In some cases the reduced imports can be attributed to increased production at home, but it should be borne in mind that shipping difficulties and the cutting off of usual sources were the controlling factors. The table is based largely upon that contained in the report of the Committee for the Chemical Industries, although a few of the allied products are from other official sources.

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS

	1913 Lbs.	1915 Lbs.	1918 Lbs.
CHEMICALS:			
Acetate of calcium, impure	5,128,781	5,740,999	1,867,976
United States	5,090,200	4,434,333	.....
Acetates and pyrolignites, n. e. s.	1,133,164	518,963	58,202
Belgium	279,984	.....	.....
France	174,825	175,487	.....
Germany	474,209	80,247	.....
United States	77,822	62,831	.....
Acetone, gallons	23,538	86,466	702,290
Germany	18,967	132	.....
United States	.....	67,207	.....
Acids (except carbolic):			
Acetic, under 90%	4,850	661	22,928
90% or more	269,182	98,325	150,576
Austria-Hungary	232,365	26,235	.....
Netherlands	1,764	33,730	.....
Impure	785,719	81,350	2,645
Austria-Hungary	740,304	64,375	.....
Arsenious	435,409	397,710	78,705
Austria-Hungary	110,010	76,720	.....
United Kingdom	215,390	261,906	.....
Boric, crude	.....	220	.....
Refined	46,076	441	.....
Carbonic	29,542	220	.....
Citric	232,144	39,462	17,637
Germany	66,580	.....	.....
United Kingdom	106,923	23,369	.....
Gallic and pyrogallic	10,803	2,205	441
Hydrochloric	87,082	29,983	.....
Lactic	111,994	23,590	441
Germany	106,042	23,590	.....
Nitric	1,314,603	.....	661
Germany	1,314,603	.....	.....
Oleic	13,578,793	17,847,780	2,594,620
France	4,041,473	7,048,548	.....
United Kingdom	5,583,150	6,721,825	.....
United States	766,318	3,873,923	.....
Oxalic	637,570	270,284	197,093
Germany	415,788	191,580	.....
United Kingdom	216,050	30,203	.....
Phosphoric	87,082	29,983	29,100
Stearic	2,028,893	933,648	335,323
France	1,259,268	311,951	.....
Netherlands	229,058	67,460	.....
United States	2,205	190,918	.....
Sulfuric	216,051	441	2,425
Sulfurous	268,961	7,055	.....
Tannic, impure	24,028,376	18,064,713	33,563,170
Argentina	8,328,980	11,931,075	.....
France	8,936,346	1,130,739	.....
United Kingdom	1,464,736	3,399,714	.....
United States	16,975	1,294,541	.....
Germany	3,270,524	82,673	.....
Pure	218,035	109,128	51,588
Germany	164,022	79,366	.....
United States	441	29,542	.....
Tartaric	88,625	192,462	5,512
Austria-Hungary	16,314	43,872	.....
France	64,815	90,609	.....
Fatty acids, solidifying at a temperature of 40°–48° C	751,107	544,095	181,000
United Kingdom	306,000	391,537	.....
United States	59,965	152,558	.....
Acids, n. e. s.	1,044,540	345,461	.....
Austria-Hungary	15,212	164,905	93,476
Germany	752,430	63,933	.....
Switzerland	215,830	36,155	.....
Alcohol, amyl, gal	79	740	.....
Methyl, gal	7,820	7,265	26
Alkaloids, n. e. s., and their salts	42,013	58,468	58,189
Germany	35,208	20,060	.....
Switzerland	4,550	14,085	.....
United States	.....	8,214	.....
Aluminum oxide, hydrated	1,155,651	28,439	5,952
Germany	1,128,975	20,502	.....
Sulfate and compound alums	5,665,602	5,381,429	904,776
France	258,820	1,343,483	.....
Germany	3,825,426	1,148,156	.....
United States	.....	1,521,615	.....
Ammonia	426,590	29,321	220
Ammonium:			
Salts, n. e. s	2,175,279	1,332,460	53,169,760
Sulfate	47,771,257	16,757,165	5,433,292
France	699,961	972,448	.....
Germany	10,333,842	.....	.....
Russia	11,381,688	.....	.....
United Kingdom	9,903,349	15,682,643	.....
Antimony salts	188,053	46,738	46,738
Germany	159,393	28,219	.....

Imports of Chemicals and Allied Products (*Continued*)

	1913 Lbs.	1915 Lbs.	1918 Lbs.
Chemicals (*Continued*):			
Barium:			
Carbonate	110,230	333,336	.....
Germany	86,421	234,570	.....
Oxide, hydrated, crystals, commercial	299,385	.....	.....
Sulfate	3,903,244	2,908,749	2,345,497
France	1,683,653	2,263,683	.....
Germany	2,073,647	520,065	.....
Bismuth salts	9,480	22,487	32,408
Bromides	37,699	35,494	23,149
Bromine	70,768	1,323	83,335
Calcium:			
Carbide	177,250	7,716	3,086
Chloride	4,945,138	4,145,309	1,900,384
United Kingdom	3,299,404	3,783,975	.....
Chemical products, n. e. s.	14,646,481	8,402,833	14,980,409
France	2,258,172	1,093,041	.....
Germany	6,552,953	1,706,360	.....
United Kingdom	2,830,045	2,290,139	.....
United States	174,604	1,547,850	.....
Chloroform	43,210	31,967	34,392
Copper sulfate	67,130,290	31,041,429	50,486
United Kingdom	65,572,521	26,041,176	.....
United States	1,510,812	4,934,556	.....
Ethers	9,921	3,086	2,866
Glycerol	1,655,434	1,743,177	15,052,940
France	997,582	738,100	.....
Germany	434,526	15,432	.....
United Kingdom	91,050	845,905	.....
Gold and platinum salts	1,054	1,334	262
Iodides	43,651	48,060	34,613
United Kingdom	11,684	17,637	.....
United States	.....	17,857	.....
Iodine	62,611	211,421	57,761
Chile	35,494	9,480	.....
Germany	21,605	.....	.....
United States	.....	178,131	.....
Iron:			
Oxide	3,970,705	2,136,698	147,048
Spain	2,170,649	1,189,161	.....
United Kingdom	809,309	542,112	.....
Sulfate	48,060	1,764	220
Lead:			
Carbonate	347,225	42,108	5,952
Austria-Hungary	52,029	29,543	.....
United States	171,297	220	.....
Oxide	1,156,092	361,554	58,202
Germany	667,494	99,427	.....
United Kingdom	395,285	240,301	.....
Lactarine (casein)	1,011,470	957,678	2,235,486
Argentina	510,144	118,167	.....
France	121,253	833,118	.....
Germany	380,073	3,748	.....
Magnesite, calcined:			
Impure, for metallurgical uses, containing not less than 5% of ferric oxide	2,901,033	1,704,376	.....
Impure, other	139,110	74,956	167,551
Pure	8,818	2,646	11,684
Magnesium:			
Carbonate	11,023	503,972	668,000
Germany	9,039	175,927	.....
United States	.....	159,172	.....
Chloride	3,449,758	646,830	312,174
Sulfate	1,110,677	139,331	.....
Manganese sulfate	21,605	9,039	882
Mercuric chloride	8,816	220	220
Phosphorus, white and red.	153,220	274,032	537,707
United Kingdom	102,073	201,721	.....
Potassium:			
Carbonate	3,055,135	1,431,888	26,015
Chloride	15,565,819	3,458,356	1,395,746
Germany	15,444,126	3,153,901	.....
Hydroxide (caustic potash)	2,072,544	1,062,617	5,070
Belgium	600,533	.....	.....
Germany	675,930	542,332	.....
United Kingdom	641,759	313,274	.....
Nitrate	1,008,825	2,866	849,880
Germany	957,457	661	.....
United Kingdom	27,558	2,205	.....
Prussiate, yellow and red.	279,543	118,387	1,323
Germany	202,162	101,632	.....
Sulfate	20,842,068	1,983,699	.....
Germany	20,492,198	1,910,286	.....
Potassium and sodium:			
Bicarbonates	3,019,200	2,538,597	4,215,900
United Kingdom	2,885,380	2,489,435	.....
Chlorates and perchlorates	485,894	1,570,337	3,546,576
France	465,392	1,053,578	.....
Chlorides of calcium, potassium, sodium (hypochlorites)	5,824,392	1,704,173	363,100
Chromates and bichromates	14,109	1,987,226	1,287,279
Germany	9,479	17,637	.....
United States	.....	1,936,740	.....
Permanganates	94,136	125,883	146,387
Silicates, liquid or in solution	4,957,925	7,887,838	4,719,215
Solid	11,495,446	8,127,919	6,368,934
Germany	7,110,937	2,798,299	.....
United Kingdom	2,814,172	3,100,329	.....
United States	.....	1,087,750	.....
Sulfides	3,330,489	1,291,234	6,618,938
Germany	1,648,379	959,662	.....
United Kingdom	1,236,780	244,711	.....

Imports of Chemicals and Allied Products (*Continued*)

	1913 Lbs.	1915 Lbs.	1918 Lbs.
Chemicals (*Concluded*):			
Potassium, etc. (*Concluded*):			
Sulfites, bisulfites, and hyposulfites of calcium, sodium, and potassium	526,679	174,384	700,408
Germany	335,540	126,323	.....
Quinine salts	111,405	108,449	109,885
Dutch East Indies	55,114	14,892	.....
Germany	40,038	24,297	.....
United States	.....	17,919	.....
Salicylates, except those of alkaloids	57,540	33,069	93,917
Silver:			
Nitrate	1,400	1,373	227
Salts, n. e. s	542	1,631	1,170
Sodium:			
Borate (borax)	304,896	1,583,123	772,500
United Kingdom	263,890	1,480,830	.....
Carbonate	115,370,466	117,265,100	49,937,778
France	66,046,950	12,635,004	.....
United Kingdom	29,794,507	103,158,305	.....
United States	.....	776,680	.....
Hydroxide (caustic soda)			
Impure	35,875,897	47,354,588	33,547,738
United Kingdom	22,556,585	32,400,124	.....
United States	45,635	13,530,072	.....
Pure	62,170	4,409	.....
Nitrate, refined	257,497	1,102	1,015,450
Germany	256,836	1,102	.....
Sulfate	22,865,891	23,383,310	16,236,600
France	18,978,079	16,475,858	.....
United Kingdom	326,501	4,122,382	.....
Tartar:			
Cream of	74,295	230,381	.....
Germany	35,053	207,674	.....
Crude	602,082	3,112,926	32,408
Wine lees	1,010,378	1,244,068	845,693
Thorium, cerium, and zirconium salts	4,332	14,200	2,435
Austria-Hungary	3,902	5,556	.....
France	364	4,493	.....
Tin:			
Oxide	133,819	46,738	15,212
Germany	99,207	661	.....
United Kingdom	.....	46,077	.....
Perchloride	1,206,137	270,504	240,524
Germany	1,204,814	.....	.....
United States	.....	207,673	.....
Salts, other	2,205	.....	220
Zinc:			
Oxide	6,577,204	4,040,150	915,139
Belgium	1,596,130	38,582	.....
Germany	2,114,873	1,393,748	.....
United States	1,200,846	1,399,480	.....
Sulfate	1,764	220	.....
Coal-Tar Products:			
Aniline and its salts	1,350,758	97,002	384,927
Germany	1,168,658	24,471	.....
United Kingdom	61,950	67,019	.....
Benzene, toluene, xylene	1,422,200	1,467,837	1,308,594
Germany	1,274,050	440	.....
United Kingdom	44,313	1,034,850	.....
United States	.....	425,712	.....
Benzoic acid	9,039	6,834	11,905
Carbolic acid	728,620	974,213	587,090
Germany	336,642	8,598	.....
United Kingdom	370,152	886,690	.....
Dyes:			
In dry form	12,468,336	4,220,266	22,535,872
Germany	10,403,949	1,722,674	.....
Switzerland	122,348	1,849,438	.....
United Kingdom	612,879	525,800	.....
In paste or liquid	1,725,100	372,798	137,348
Germany	1,440,707	178,792	.....
United States	.....	111,994	.....
Indigo, synthetic	1,348,995	285,055	217,817
Germany	1,248,465	97,223	.....
Switzerland	98,546	187,832	.....
Naphthalene	49,604	.....	7,095,576
Germany	45,636	.....	.....
Nitrobenzene, crude	100,090	.....	.....
Saccharin	456	560	61,729
United Kingdom	317	362	.....
Salicylic acid	100,090	21,826	139,994
Germany	95,459	10,803	.....
Medicinal Preparations:			
Wines, sirups, elixirs	146,385	60,847	74,516
France	104,499	46,738	.....
Pills, granules, capsules	267,638	190,477	183,645
France	122,134	92,813	.....
United Kingdom	83,334	46,738	.....
Other	751,328	692,244	270,066
France	323,855	289,464	.....
Germany	204,146	53,131	.....
United Kingdom	144,842	157,629	.....
United States	7,937	112,655	.....
Medicinal products, n. e. s.	659,837	1,459,886	310,630
France	148,370	136,685	.....
United Kingdom	354,279	1,295,203	.....
Salts of mineral waters	87,083	35,054	.....
Oils, Vegetable:			
Fixed:			
Castor	41,888	257,720	4,906,166
Coconut	8,803,718	6,728,066	3,984,193
Linseed, boiled	597,010	3,017,907	1,023,165
Raw	388,234	1,813,082	1,766,784
Palm	11,913,339	.....	.....
Peanut	7,633,284	2,233,943	.....
Other	30,283,358	39,874,560	2,217,629

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Continued*)

	1913 Lbs.	1915 Lbs.	1918 Lbs.
OILS, VEGETABLE (*Concluded*):			
Volatile:			
Clove	4,230	2,612	2,505
Essences of citrus fruits	6,184	4,242	161
Peppermint	12,350	8,580	15,100
Rose	575	359	818
Other	244,565	202,274	156,880
PAINTS, PIGMENTS, VARNISHES, ETC.:			
Black:			
Bone black	1,867,737	2,186,743	148,812
France	82,452	1,468,264	.....
Germany	1,168,218	3,307	.....
Lampblack	606,045	835,764	212,746
France	175,266	381,395	.....
Germany	182,760	147,929	.....
United States	129,851	186,730	.....
Other	1,078,931	472,005	96,562
France	107,805	84,657	.....
Germany	807,104	289,243	.....
Color, n. e. s.	4,516,123	1,517,867	747,367
France	361,554	241,404	.....
Germany	3,410,516	911,601	.....
United Kingdom	320,990	221,342	.....
Indigo, natural	125,442	112,214	156,308
Varnishes:			
Alcoholic	30,864	9,921	27,778
Non-alcoholic, containing mineral oil	2,096,795	1,285,061	725,760
Germany	692,906	121,694	.....
United Kingdom	782,192	604,722	.....
United States	204,587	279,103	.....
Other	4,384,729	2,377,661	265,877
France	1,313,280	1,373,246	.....
Germany	1,639,340	159,834	.....
United Kingdom	1,084,222	679,678	.....
OTHER ALLIED PRODUCTS:			
Blacking and shoe polishes:			
In boxes, vials, and the like	2,108,039	498,019	.....
Belgium	1,344,586	265,435	.....
Germany	598,990	212,965	.....
In other containers	39,462	32,849	.....
Candles:			
Paraffin, or of stearin combined with more than 30% of paraffin	58,422	42,549	43,652
Stearin	35,274	9,480	18,298
Dyeing extracts	1,070,554	4,332,259	.....
France	257,497	1,551,377	.....
United Kingdom	351,634	1,000,227	.....
United States	294,335	1,631,183	.....
Explosives:			
Blasting powder	5,512	.....	215,170
Gunpowder, for hunters	3,748	9,921	.....
Other explosives	62,611	2,393,755	75,350,900
France	2,425	1,651,686	.....
United States	.....	712,086	.....
Fertilizers:			
Chemical	159,233,849	30,326,478	361,558
France	46,422,262	13,139,416	.....
Germany	27,209,173	1,688,724	.....
Greece	18,137,244	3,981,508	.....
Tunis	30,379,388	2,050,278	.....
Chile saltpeter	148,630,350	158,137,118	213,875,266
Phosphate rock	116,795,600	100,729,416	51,076,474
Thomas slag	262,916,688	2,601,454	220,462
Glucose:			
Liquid	515,220	1,355,826	6,691,250
Solid	1,323	441	26,896
Glue:			
Common	3,384,757	1,256,193	146,166
Fish glue	23,589	29,100	17,417
Imitation	363,542	306,220	32,408
Greases, lubricating	512,574	54,224	727,525
Gums and resins:			
Camphor, refined	79,586	206,130	48,280
Rosin	39,918,031	54,540,922	23,266,477
France	2,713,422	4,866,875	.....
Greece	2,487,230	4,689,625	.....
United States	33,911,157	38,900,828	.....
Other native gums and resins	982,600	472,010	578,493
Gums and resins, n. e. s.	4,743,025	3,124,610	3,284,446
Inks:			
Printing	524,254	281,087	125,884
France	160,715	163,581	.....
Germany	323,195	70,768	.....
Other	790,129	306,439	130,073
France	295,638	124,118	.....
Germany	242,947	64,815	.....
Manna	441	3,748	.....
Perfumes:			
Alcoholic	411,600	281,968	172,622
France	200,398	148,590	.....
Germany	171,077	83,334	.....
Non-alcoholic	583,117	436,511	229,942
France	293,654	244,712	.....
Germany	160,274	82,893	.....
Petroleum jelly:			
Natural	99,648	218,255	417,776
Germany	73,855	.....	.....
United States	20,282	126,102	.....
Artificial	141,535	36,596	334,440
Germany	72,090	661	.....
United Kingdom	32,408	441	.....
United States	1,984	18,739	.....
OTHER ALLIED PRODUCTS (*Concluded*):			
Soap:			
Common	12,541,528	5,726,449	18,921,390
France	11,378,381	4,022,954	.....
United Kingdom	634,925	1,524,260	.....
Glycerol	58,863	26,235	19,621
United Kingdom	24,030	20,063	.....
Scented	458,336	242,947	3,397,100
Germany	197,973	18,960	.....
United Kingdom	162,259	167,108	.....
United States	8,598	13,448	.....
Tar, vegetable	3,485,288	1,123,475	4,973,628
Turpentine, spirits of	7,640,120	6,967,268	4,842,894
Waxes:			
Ceresin	167,991	88,184	10,582
Austria-Hungary	97,224	50,044	.....
Germany	69,004	30,644	.....
Paraffin, solid	54,318,037	71,508,406	38,649,895
Austria-Hungary	20,008,509	411,158	.....
Russia	7,196,696	.....	.....
United Kingdom	6,056,477	8,565,973	.....
United States	18,717,495	60,426,543	.....

EXPORT STATISTICS

Details of Italy's chemical exports are shown in the following table, which, with the exception of the figures for sulfur, is also taken from the report of the Committee for the Chemical Industries:

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS

	1913 Lbs.	1915 Lbs.	1918 Lbs.
CHEMICALS:			
Acids:			
Acetic, pure	683,433	298,726	141,316
Boric, crude	1,700,866	809,978	275,357
United Kingdom	471,569	318,567	.....
United States	368,172	429,020	.....
Boric, refined	1,258,839	2,612,698	2,663,625
United Kingdom	778,232	2,351,010	.....
Carbonic	100,972	181,220	52,029
Citric	486,119	1,665,590	1,661,844
France	29,321	246,918	.....
United Kingdom	53,672	421,303	.....
United States	8,818	230,825	.....
Hydrochloric	119,050	716,723	2,142,010
Oleic	5,726,725	2,468,295	.....
Sulfuric	331,795	15,568,160	2,235,928
France	.....	14,804,920	.....
Malta	90,390	289,908	.....
Tannic, impure	56,323,470	11,318,968	918,225
Germany	16,343,527	1,750,910	.....
Switzerland	1,532,653	1,513,694	.....
United Kingdom	17,783,365	4,508,673	.....
Tartaric	6,274,795	8,012,480	4,345,310
France	429,020	837,536	.....
United Kingdom	1,983,720	2,940,967	.....
United States	62,611	278,000	.....
Aluminum sulfate and compound alums	1,918,021	130,073	338,189
Barium:			
Carbonate	.....	303,360	26,455
Sulfate	516,543	7,248,356	1,152,797
Switzerland	46,958	2,937,439	.....
United Kingdom	1,764	3,720,300	.....
Calcium:			
Carbide	24,332,858	11,314,563	30,203
Portugal	5,438,140	3,400,850	.....
United Kingdom	16,265,704	3,706,630	.....
Citrate	8,406,000	14,779,790	8,235,807
France	2,103,650	2,750,487	.....
United Kingdom	1,946,240	3,712,143	.....
United States	2,561,110	7,263,569	.....
Carbon bisulfide	1,904,794	1,208,897	718,486
Chemical products, n. e. s.	2,806,043	1,717,180	526,464
Copper sulfate	1,151,695	13,889	705,479
Glycerol	2,775,178	87,964	441
Iron:			
Oxide	300,785,626	42,941,190	97,849,517
France	35,204,957	18,237,077	.....
United Kingdom	196,859,545	24,691,770	.....
Sulfate	191,140	122,797	34,833
Lead carbonate	465,837	680,567	2,425
Magnesia, calcined, pure	483,915	701,290	627,435
Calcined, impure	2,273,627	2,364,017	302,254
France	590,618	1,544,779	.....
United States	.....	662,269	.....
Magnesium:			
Carbonate	79,366	1,131,192	298,285
Sulfate	40,785	54,013	1,764
Mercuric salts, n. e. s.	20,282	126,325	12,346
Phosphorus, red and white	.....	.....	1,361,133
Potassium and sodium chlorates and perchlorates	49,163	47,620	13,665,350
Potassium, sodium, and calcium chlorides (hypochlorites	1,560,873	584,885	88,195
United Kingdom	.....	445,775	.....
Quinine salts	59,935	780	280
Sodium carbonate	741,635	206,794	55,336
Tartar:			
Cream of	767,208	3,208,828	1,333,135
Australia	31,306	1,438,075	.....
United Kingdom	601,420	1,169,993	.....

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Continued*)

	1913 Lbs.	1915 Lbs.	1918 Lbs.
CHEMICALS (*Concluded*):			
Tartar (*Concluded*):			
Crude	18,286,460	17,409,682	15,011,715
United Kingdom	3,714,127	4,583,630	.....
United States	8,772,192	10,488,270	.....
Wine lees	9,400,289	5,270,149	2,295,893
Thorium, cerium, and zirconium salts	.....	320	13,726
Zinc oxide	2,895,770	5,643,392	164,464
United Kingdom	2,004,000	4,810,706	.....
COAL-TAR PRODUCTS:			
Naphthalene	274,255	661,387	102,074
OTHER PRODUCTS:			
Blacking and shoe polishes	395,950	265,657	13,448
Candles:			
Paraffin, and paraffin mixed with stearin	4,807,400	11,273,777	119,931
Argentina	761,697	1,700,866	.....
Germany	.....	6,808,535	.....
Stearin	84,657	545,424	33,730
Dyeing and tanning materials:			
Sumac, ground	34,184,437	34,529,678	24,215,789
France	5,443,433	4,613,172	.....
United Kingdom	13,799,393	12,165,106	.....
United States	8,469,718	14,530,886	.....
Sumac, not ground	18,120,010	12,508,366	19,218,628
Fertilizers, chemical	43,001,163	28,494,746	13,228
Austria-Hungary	16,215,000	5,833,430	.....
Switzerland	12,489,185	16,609,625	.....
Glue, common	2,436,770	4,217,663	3,394,457
Ink:			
Printing	20,062	194,668	19,621
Other	122,356	150,575	473,332
Manna	770,736	509,268	453,932
Brazil	183,204	142,860	.....
France	78,485	66,800	.....
United States	87,964	66,139	.....
Medicinal preparations:			
Pills, pellets, capsules	332,898	184,086	135,364
Wines, sirups, elixirs	43,652	135,584	69,887
Other	2,474,468	1,245,390	523,156
Medicinal products, n.e.s.	425,050	134,702	109,570
Oils, vegetable:			
Fixed:			
Castor oil	1,169,552	672,189	207,675
Argentina	221,785	247,579	.....
Germany	4,409	77,162	.....

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Concluded*)

	1913 Lbs.	1915 Lbs.	1918 Lbs.
OTHER PRODUCTS (*Concluded*):			
Oils, vegetable (*Concluded*):			
Volatile or essential:			
Bergamot	139,096	232,704	1,811,778
France	62,335	85,650	.....
United States	22,130	57,461	.....
Essences of citrus fruits, n. e. s.	2,639	935	2,747
Lemon	1,007,303	1,640,263	3,592,961
Germany	101,175	61,848	.....
United Kingdom	232,169	591,568	.....
United States	426,186	562,770	.....
Mandarin	2,013	2,661	4,766
Orange	106,050	155,805	689,650
United Kingdom	23,913	28,786	.....
United States	26,193	47,384	.....
Peppermint	49,152	50,353	21,684
Other	31,495	38,387	51,275
Paints, pigments, colors, varnishes:			
Colors, n. e. s.	1,871,724	2,666,930	2,498,940
Varnishes, non-alcoholic	586,650	428,800	533,077
Soap:			
Common	6,808,976	23,180,276	869,944
Austria-Hungary	106,704	4,776,314	.....
Germany	12,346	11,496,444	.....
United States	2,371,512	2,307,798	.....
Scented	5,639,423	315,702	54,454
	1913 Metric tons	1915 Metric tons	1918 Metric tons
Sulfur:			
Crude	212,143	190,459	.....
Refined	49,375	28,802	.....
Ground	85,427	65,459	.....
Flowers of sulfur	4,394	9,188	.....
Total exports	351,339	293,908	.....
Australia	13,447	358	.....
Austria-Hungary	40,981	16,162	.....
British South Africa	13,761	9,821	.....
France	76,036	99,090	.....
Germany	38,979	26,378	.....
Greece	14,190	19,109	.....
Portugal	14,777	12,779	.....
Russia	25,352	2,791	.....
Sweden	19,541	17,992	.....
United Kingdom	16,465	36,880	.....
United States	1,028	1,845	.....

ORIGINAL PAPERS

ON THE ABSORPTION OF OXIDES OF NITROGEN BY NITRIC ACID

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Received December 8, 1919

INTRODUCTION

A number of researches[1] have been published dealing with the mechanism of the absorption of nitrogen dioxide by water or by dilute nitric acid. Perfect unanimity of opinion based on the results of experiments conducted under varying conditions has, however, by no means been arrived at, nor has it been found possible to explain the phenomena occurring in nitric acid condensing towers as operated under technical conditions. The following series of experiments was accordingly undertaken to investigate in more detail the mechanism of absorption under conditions approximating those which actually obtain in practice, with a view to gaining information on the optimum conditions of absorption by water and nitric acid of various concentrations, so as to explain the mechanism of operation and render the scientific design of absorption towers possible.

The experiments of Foerster and Koch[1] have indicated that the primary reaction between nitrogen dioxide and water can be expressed by means of the reversible equation

$$2NO_2 + H_2O \rightleftarrows HNO_2 + HNO_3, \qquad (1)$$

a view which was confirmed by Briner and Durand.[2]

This reaction, however, does not seem to explain the whole phenomenon of the absorption process, since it is found by experiment that equivalent quantities of nitrous acid are not obtained in nitric acid produced either in the laboratory or in absorption towers by the passage of nitrogen dioxide into water. To account for this deficiency in nitrous acid two theories have been advanced, the theory of volatilization by Foerster and Koch, and the view advanced by Saposhnikoff[3] and by Lewis and Edgar[4] that the removal is effected by secondary decomposition.

Since nitrous acid is appreciably more volatile than nitric acid, Foerster and Koch assumed that its removal was effected by the air current. Under these conditions the equilibrium resulting from Equation 1 is disturbed and relatively strong solutions of nitric acid can be obtained. That a limit is set to the strength of nitric acid obtainable in this manner is a point which will be referred to later. Lewis and Edgar, and Saposhnikoff, on the other hand, assume that nitrous acid undergoes decomposition according to one of the following equations:

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[1] In a recent communication on the theory of absorption towers for nitric acid manufacture, Partington and Parker (*J. Soc. Chem. Ind.*, **38** (1919), 75), with the permission of the British Munitions and Inventions Board, have translated into technical figures certain data which were derived by the writer from experimental and theoretical considerations W. R. Bousfield (*J. Chem. Soc.*, **115** (1919), 45) has likewise made use of the hypothesis then privately advanced to explain certain peculiarities in this series of the reactions. It consequently appears desirable to record the experimental work on which the above-mentioned data have been founded.

[1] *Z. angew. Chem.*, **21** (1908), 2161.

[2] *Compt. rend.*, **155** (1912), 582, 1445.

[3] *J. Russ. Chem. Soc.*, **32** (1901), 375; **33** (1901), 506.

[4] *J. Am. Chem Soc.*, **2** (1901), 1330; **33** (1911), 292

$$3HNO_2 \rightleftarrows HNO_3 + 2NO + H_2O \qquad (2)$$

$$2HNO_2 \rightleftarrows NO + NO_2 + H_2O \qquad (3)$$

The first reaction, based on Lewis and Edgar's work, is extremely improbable, being essentially a termolecular reaction. Experiments by Saposhnikoff and these authors were made in order to determine the equilibrium constant of Equation 2. The values for K where

$$K = \frac{C^2_{NO}C_{H^+}}{C^3_{HNO_2}}$$

gave exceedingly un-uniform results varying in one series of experiments from 0.0545 to 0.0287 with changing concentrations. Equation 3 may be criticized in that equal volumes of nitric oxide and nitrogen dioxide resulting from the dehydration of nitrous acid would react to form the anhydride of nitrous acid, N_2O_3, a gas perfectly stable under the conditions of the experiment. This alternative suggestion gives no explanation as to why a limit is set to the nitric acid strength (from 50 to 64 per cent) when nitrogen dioxide and air are passed continuously into water.

ABSORPTION OF NITROGEN DIOXIDE BY DILUTE NITRIC ACID IN THE PRESENCE OF AIR

Preliminary experiments on the reaction velocity indicated that it took place with considerable speed, and that the methods of injecting water into a dry gaseous NO_2-air mixture or of collecting a sample of the dry mixture over water and noting the decrease in volume were inapplicable, due in the first instance to the relatively slow rate at which water vaporizes to exert its maximum vapor pressure at the desired temperature, and in the second to absorption during the process of filling.

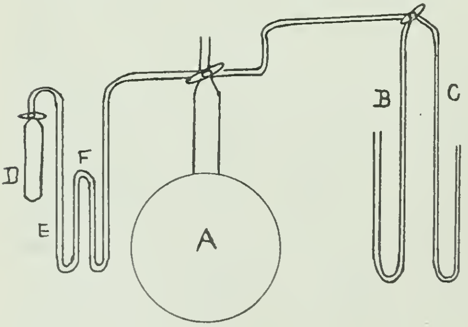

FIG. 1

METHOD—The following procedure led to uniform and consistent results (Fig. 1). A 200-cc. flask, A (approximating to the volume of a Gutmann ball, the standard packing for nitric acid absorption towers), connected to a 3-way cock, was immersed in a thermostat at the desired temperature, 5 cc. of water or dilute nitric acid were introduced, and the contents allowed to come to equilibrium with the vapor and air. A slight vacuum was then produced in the flask, the amount being registered in the duplicate gauges B and C, B being a mercury column with the mercury protected by a layer of high-boiling paraffin oil, the fine gauge C being filled with paraffin. All taps were lubricated with phosphoric acid. The requisite amount of nitrogen dioxide was then admitted as vapor from a small flask, D, containing purified liquid nitrogen dioxide, through the capillary heating tube EF. This operation could be performed in from 2 to 3 sec. Readings were made with reference to an arbitrary mark on the manometer.

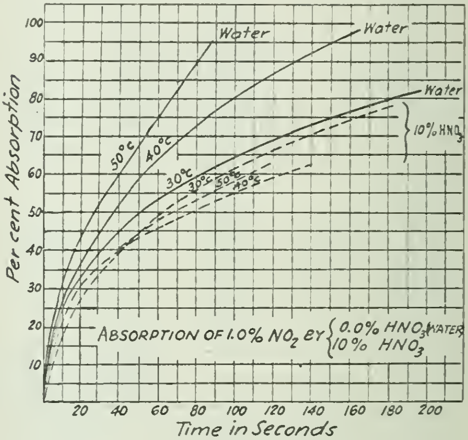

FIG. 2

The percentage absorption was calculated on the assumption that the contraction in volume was due to the removal of oxygen and nitrogen dioxide from the gaseous phase in the following proportions:

$$4NO_2 + O_2 = 2N_2O_5 \qquad (4)$$

it being assumed that the quantity of nitrous acid formed as a permanent constituent under the conditions of the experiment according to Equation 2 was negligibly small, although the intermediate formation of nitrous acid with its subsequent oxidation is not negatived. Later experiments confirmed this assumption.

The results of such determinations using 10, 5, and 1 per cent NO_2-air mixtures with nitric acid solutions of 50, 25, 10, and 8 per cent strength at temperatures of 30°, 40°, and 50° C., are depicted in Figs. 2 to 6.

DISCUSSION OF CURVES—From a study of these curves in the light of the following considerations some insight into the mechanism of absorption may be obtained.

It is evident that the absorption of nitrogen dioxide in strong nitric acid proceeds most rapidly at low temperatures, while the absorption in water proceeds most rapidly at high temperatures. The point of inversion, *i. e.*, where the absorption rate is practically independent of the temperature, is in the neighborhood of 10 per cent nitric acid. The dependence of the absorption rate on the partial pressure of the nitrogen dioxide is clearly brought out, thus negativing the statement frequently made that a 5 per cent NO_2-air mixture exhibits the maximum velocity of absorption.

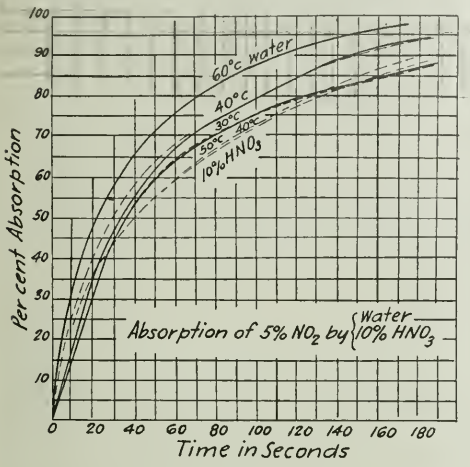

FIG. 3

It is usually assumed that reaction takes place between the monomolecular form of nitrogen dioxide and water, but there exists the possibility that a similar hydration may take place with the bimolecular form N_2O_4, with which the nitrogen dioxide is in equilibrium.

TABLE I

Total Pressure NO_2 Mm. Mercury	Pressure N_2O_4 30° C.	50° C.
10	0.342	0.279
20	1.252	1.477
30	2.814	2.320
40	4.800	3.999
50	7.195	5.596
60	9.948	8.349
70	12.02	11.02
80	16.40	13.92
90	20.023	17.10

Table I calculated from the van't Hoff equation

$$\log \frac{K_{T_2}}{K_{T_1}} = -\frac{Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where K_T is the equilibrium constant of the reaction at T°

$$2NO_2 \rightleftarrows N_2O_4 \qquad (5)$$

indicates that the quantity of polymerized nitrogen dioxide present under the conditions of the experiment is by no means negligible. The value of Q adopted is

$$2NO_2 = N_2O_4 + 12{,}600 \text{ cal.}$$

It will be noted that the partial pressure of the N_2O_4 rises rapidly with increasing pressure and decreasing temperature. It is evident, therefore, that the reaction may occur in either of two ways or simultaneously

$$2NO_2 + H_2O \rightleftarrows HNO_3 + HNO_2 \qquad (6)$$

$$N_2O_4 + H_2O \rightleftarrows HNO_3 + HNO_2 \qquad (7)$$

with subsequent oxidation of the nitrous acid formed. Assuming the water to be present in large excess, the reaction should be mono- or bimolecular according as N_2O_4 or NO_2 is the reacting constituent.

Applying van't Hoff's partial differential method of analysis to the curves giving the absorption of the oxides in water at 50° C., we obtain, if c and c' be two different gas concentrations and $\frac{dc}{dt}$ and $\frac{dc'}{dt}$ their respective rates of solution, the order of the reaction n by means of the following expression:

$$\frac{\log \frac{dc}{dt} - \log \frac{dc'}{dt}}{\log c - \log c'} = n$$

Inserting the values obtained from the curve,

$$\frac{dc}{dt} = \frac{0.1}{18.5} \text{ at } c = 0.25$$

$$\frac{dc}{dt} = \frac{0.1}{5.8} \text{ at } c = 0.65$$

$$n = \frac{0.5031}{0.515} = 0.97$$

i. e., the reaction is monomolecular.

The absorption rate may therefore depend on the actual gas pressure of the NO_2 molecules, being limited by the rate of diffusion, thus being a pseudo-monomolecular chemical reaction, or it may depend on the N_2O_4 concentration alone, being a pure monomolecular chemical reaction. The figures given in Table II for the times of half completion of reaction at various concentrations of gas and solvent show that both take place.

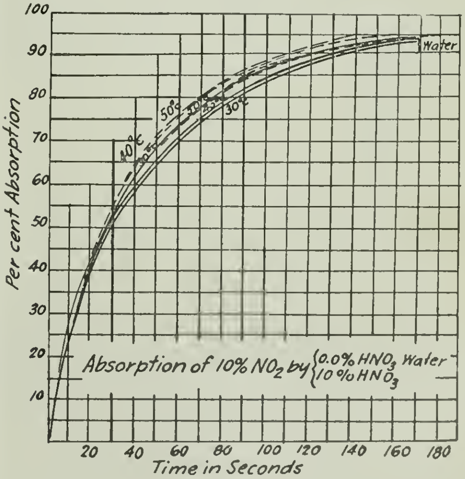

FIG. 4

It is evident that neither set of figures exhibits constancy for varying nitrogen dioxide concentrations under similar conditions of temperature and nitric acid concentration, but it may be deduced that for solution in water the reaction velocity is practically

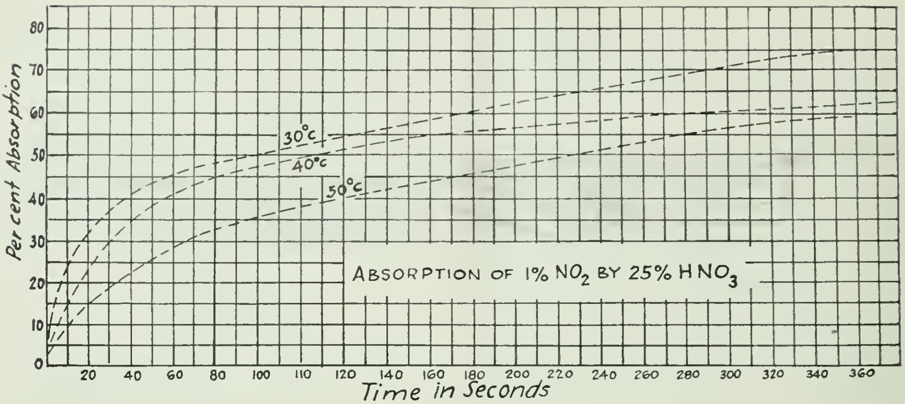

FIG 5

proportional to the NO_2 and not to the N_2O_4 partial pressure, *i. e.*, it is limited practically entirely by the rate of physical absorption. For absorption in nitric acid the conditions are not the same, for as the concentration of the acid increases the reaction becomes more chemical in character. An increase in gas pressure is also associated with a transition from a physical to a chemical type of change. From these considerations the reaction velocity in the strong acid towers may be taken as governed chiefly by the concentration of the N_2O_4 molecules, while in the weak acid towers where the gas is less concentrated the reaction velocity is governed by the physical rate of absorption.

TABLE II

HNO_3 Per cent	Temp. ° C.	NO_2 Per cent	N_2O_4 Per cent	Time for Half Completion in Form of NO_2	Time for Half Completion $\times \frac{N_2O_4}{NO_2}$
0	30	1	0.034	51	1.73
		5	0.544	36	3.91
		10	2.05	28	5.75
0	50	1	0.029	27	0.784
		5	0.451	24	2.16
		10	1.75	25	4.37
25	30	1	0.039	96	3.27
		5	0.544	33	3.54
		10	2.05	30	6.16
25	40	1	0.031	110	3.414
		5	0.498	44	4.38
		10	1.90	37	7.04
25	50	1	0.029	220	6.4
		5	0.451	122	11.0
		10	1.75	71	12.4
50	30	5	0.544	97	10.55
		10	2.05	42	8.01

In the usual 36-in. stoneware towers the inflowing gas is maintained at between 30° and 60° C., according to the various authorities. The optimum is stated to be 40° C., since under these conditions the heat total of all the reactions summarized

$$4NO_2 + O_2 + 2H_2O = 4HNO_3$$

just balances the heat loss by radiation, and the gas and liquid temperature is said to be practically uniform in all the towers. From the above experiments, however, it would appear that better results could be obtained by cooling the entering gases to a still lower temperature and warming the weak acid towers to above 40° C.

If we assume that the opportunity factor of liquid gas contact is the same in the spherical flask as in a Gutmann ball situated in the packing of a tower we may make a rough approximation as to the efficiency of various tower systems by calculating the percentage removal for different acid strengths at varying temperatures from the curves. In Table III such calculations are made, assuming the entering gas to contain 10 per cent NO_2 and to vary in temperature *per saltum* from 30° C. to 50° C. from the first to the last tower. The acid strength is assumed to vary from 0 per cent in the last tower to 55 per cent in the first.

TABLE III

Time of Contact		Percentage Removal by Tower System		
Min.	Sec.	4 Towers	6 Towers	8 Towers
0	..	0.0	0.0	0.0
1	0	68.0	74.0	81.0
1	30	..	89.0	..
2	0	82.5	92.5	94.3
2	30	..	95.0	..
3	0	94.4	96.5	97.7

It will be noted that these figures approximate the results actually obtained in practice; further, if it be assumed that the interior of the flask is completely moistened by the nitric acid and that reaction occurs on the wet surface of the glass (0.178 sq. ft.), we may calculate the absorption rate per sq. ft. of tower surface, obtaining with a 10 per cent gas a figure of approximately 2×10^{-4} lbs. NO_2 per min. per sq. ft. of surface. In the operation of three towers of a total capacity of 12,000 cu. ft. and a superficial area per cu. ft. of packing of 15 sq. ft. with a 10 per cent NO_2 gas, 34 lbs. of nitrogen dioxide were absorbed per minute during a long run, or 1.99×10^{-4} lbs. NO_2 per min. per sq. ft., giving an excellent agreement with the calculated figure.[1]

The influence of nitric acid concentration on the rate of absorption can also be calculated from the curves. If we assume that the general equation

$$N_2O_4 + H_2O \rightleftharpoons HNO_3 + HNO_2$$

is reversible, the velocity of absorption of nitrogen dioxide is given by

$$\frac{Dc}{Dt} = K.C_{N_2O_4}.C_{H_2O} - K.C_{HNO_2}.C_{HNO_3}$$

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[1] Partington and Parker, *Loc. cit.*

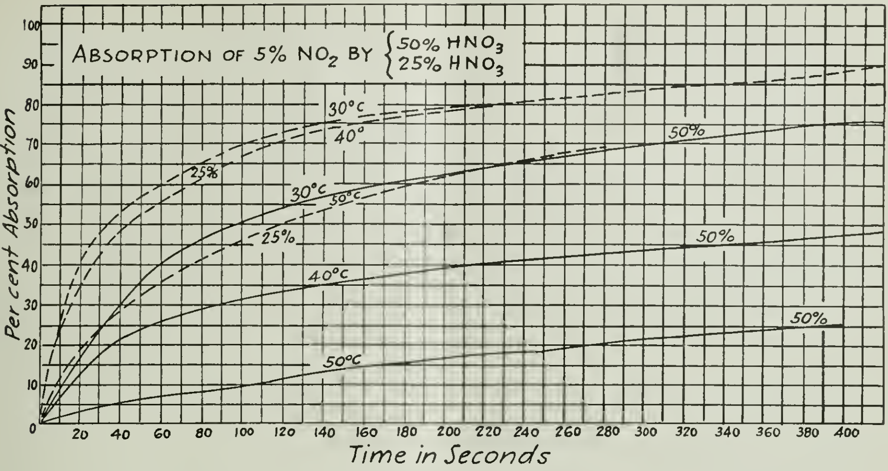

FIG. 6

Then, provided that the HNO_2 functions in solution as nitric acid, *i. e.*, its rate of conversion into nitric acid being comparable to the above reaction velocity, we may write the above equation, for a constant concentration of nitrogen dioxide and with water in relatively large excess,

$$\frac{Dc}{Dt} = \alpha - \beta C^2_{HNO_3}, \text{ where } \alpha \text{ and } \beta \text{ are constants.}$$

In Table IV are given the experimental results.

TABLE IV

	$\frac{Dc}{Dt}$	C^2HNO_3	$\alpha - \beta C^2$
10 per cent gas at 40° C...........	1.08	0.0	(1.08)
	1.0	0.01	1.04
	0.65	0.062	0.83
	0.09	0.25	(0.09)
10 per cent gas at 30° C...........	0.96	0.0	(0.96)
	0.95	0.01	0.94
	0.83	0.062	0.84
	0.52	0.25	(0.62)
1 per cent gas at 30° C............	0.79	0.0	(0.79)
	0.80	0.01	0.77
	0.51	0.062	0.64
	0.20	0.25	(0.20)

It will be noticed that there is a fair agreement between the observed and calculated figures. Even better results are obtained, however, when this equation is applied to the experimental figures obtained from actual tower operation. The observed and calculated values for the rate of absorption of nitrogen dioxide in a set of towers are given below.

$\frac{Dc}{Dt}$	C_{HNO_3} Per cent	$\frac{Dc}{Dt}$ (Calculated from $\alpha - \beta C^2$ where $\alpha = 1.00$; $\beta = 1.25$)
1.00	0	(1.00)
0.99	10	0.99
0.95	20	0.94
0.90	30	0.89
0.80	40	0.80
0.70	50	0.69
0.55	60	(0.55)
0.32	65	0.48
0.00	68	0.32

The calculated values between the limits

C_{HNO_3} = 0 per cent and C_{HNO_3} = 60 per cent

are excellent, but for stronger acid strengths when the concentration of water becomes smaller, bigger discrepancies, as would be expected, are noticed.

ELIMINATION OF NITROUS ACID

As the product of interaction of nitrogen dioxide and water, nitric and nitrous acids are formed in equivalent quantities, but as the acidity of the solution increases, a greater deficiency of nitrous acid is observed; for example, with 50 per cent nitric acid the following figures (Table V) for the nitrous acid content were obtained by two methods:

(*a*) After aspiration of a NO_2-air mixture through a nitric acid solution in a thermostat.

(*b*) After aspiration of a NO_2-air mixture through a nitric acid solution to which nitrous acid had been added so as to obtain a relatively supersaturated solution of the latter in nitric acid.

TABLE V

TEMPERATURE ° C.	PARTS PER THOUSAND HNO_2 (*a*)	HNO_2 (*b*)
18	1.20	1.26
40	0.32	0.50
50	0.10	0.18

It will be noted that equilibrium is practically reached whether nitric acid or nitric-nitrous acid mixtures are employed to start with.

From the previously recorded experiments it appeared possible to explain the mechanism of the absorption process in nitric acid towers by means of two reactions which would serve to explain the fundamental difficulty associated with the alternative theories already alluded to, *viz.*, the limitation of the acid strength to 68 per cent. As has already been pointed out, the primary reaction on solution occurs according to the equation

$$N_2O_4 + H_2O = HNO_3 + HNO_2.$$

In the presence of even dilute nitric acid, nitrous acid is unstable and breaks up into its anhydride and water.

$$2HNO_2 = N_2O_3 + H_2O.$$

The nitrogen trioxide thus produced is in solution and not immediately eliminated, but is removed in one of two ways:

(1) In the gas phase or in solution by means of dissolved oxygen according to the equation

$$2N_2O_3 + O_2 = 2N_2O_4.$$

(2) In solution, by reaction with the nitric acid according to the equation

$$N_2O_3 + 2HNO_3 = 2N_2O_4 + H_2O.$$

(1) ELIMINATION BY OXIDATION—The rate of oxidation of nitric oxide to nitrogen dioxide by means of oxygen in the gas phase has been studied by Lunge and Berl,[1] Foerster and Blick,[2] and more recently by Bodenstein and E. Briner.[3] The reaction possesses a negative temperature coefficient and is relatively slow. The necessity of providing space and time for this secondary oxidation as well as of maintaining the gases at low temperature has been generally recognized.

No investigations appear to have been carried out on the reaction velocity when in solution in water or dilute nitric acid. Such reactions proceed generally more rapidly in solvents than in the gaseous phase, and it would appear from some of Cavendish's experiments on the estimation of oxygen by means of nitric oxide in a eudiometer that this is no exception. The matter is of considerable technical importance in the design of Pohle air or oxygen lifts for nitric acid towers.

(2) ELIMINATION BY INTERACTION WITH NITRIC ACID—If this hypothesis of possible interaction be correct, it is evident that less nitrogen trioxide will be eliminated to be oxidized by atmospheric oxygen according to the first reaction, owing to the fact that it has been practically all removed by interaction with the nitric acid.

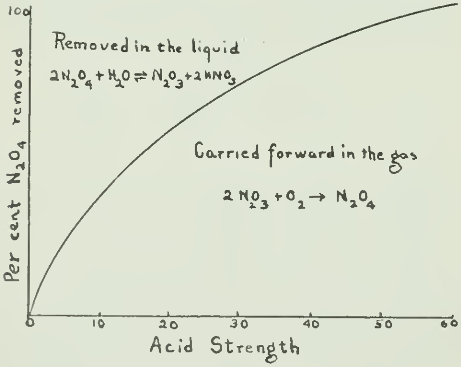

FIG. 7

The mechanism of the tower reaction can be depicted graphically as in Fig. 7.

It will be noted that the reaction in the gas phase is practically irreversible at normal temperatures, but in the liquid phase it is a truly reversible reaction.

In support of the hypothesis that nitric acid can be reduced to nitrogen dioxide by nitrogen trioxide according to the equation[1]

$$N_2O_3 + 2HNO_3 = 2N_2O_4 + H_2O$$

it may be urged that Fritzsche[2] showed that the addition of N_2O_4, cooled to —20° C., to water was attended with a separation into two layers both containing the deep blue nitrous anhydride and nitric acid, and that with increasing temperature there was an increase in the evolution of nitrogen trioxide, supporting the assumption that the formation of N_2O_3 from the N_2O_4 and water is a primary reaction. The addition of liquid N_2O_4 to nitric acid of 65 per cent and under at 20° C. was attended by a vigorous reaction and the formation of the blue liquid, nitrous anhydride. Acid over 70 per cent in strength when similarly treated yielded no blue liquid, indicating that the equilibrium is shifted over to the right by the mass of the nitric acid. Ramsay likewise prepared pure N_2O_4 by the interaction of N_2O_3 and strong nitric acid. Using 100 per cent nitric acid N_2O_4 can actually be distilled off without the use of any other dehydrating agent.

Fritzsche's results were confirmed by experiment and attempts were made to find the equilibrium constant of the reaction

$$2N_2O_4 + H_2O = 2HNO_3 + N_2O_3.$$

A definite amount of N_2O_4 was added to nitric acid of various strengths and after completion of the reaction the N_2O_3 and N_2O_4 were extracted with pentachlorethane. The partition coefficient of nitric acid between water and pentachlorethane having been previously determined, and assuming that both N_2O_3 and N_2O_4 have approximately the same partition coefficient between solvent and nitric acid, the ratio of N_2O_3 to N_2O_4 could be determined by titration of the pentachlorethane layer with alkali and permanganate. The following results were obtained:

Strength of Acid Per cent	Ratio $N_2O_3 : N_2O_4$	$K = \frac{C^2_{N_2O_4}\, C_{H_2O}}{C_{N_2O_3}\, C^2_{HNO_3}}$
68.0	1 : 10.55	0.90
66.7	1 : 8.51	0.75
58.6	1 : 7.17	0.99

A series of further experiments with varying amounts of nitrogen dioxide gave the following values for K:

Acid Strength	K
68.0	0.78
66.7	0.75
64.7	0.80
56.6	0.93
MEAN	0.815

The constancy of K is only approximate and is probably due to the loss of nitric oxide into the air space above the liquid, but the decreasing concentration of N_2O_4 in equilibrium with a given quantity of N_2O_3 in the presence of increasingly dilute acid is demonstrated from the above figures.

The following example shows the method of procedure: Five cc. of 58.6 per cent acid were placed in a small separatory funnel and 0.30 cc. (0.4425 g.) of purified liquid N_2O_4 was added and allowed to attain equilibrium, with agitation. The solution was then shaken with 5 cc. of pentachlorethane which was subsequently run into 10 cc. of 0.958 *N* caustic soda. In the present case back titration required 3.3 cc. of 1.064 *N* sulfuric acid.

---

[1] *Z. angew. Chem.*, **19** (1906), 801.

[2] *Ibid.*, **23** (1910), 2017.

[3] *Arch. des Sciences*, **46** (1918), 23.

[1] It is interesting to note that the strongest nitric acid obtained in practice corresponds to the formation of the dihydrate $HNO_3.2H_2O$.

[2] *J. prakt. Chem.*, **22** (1841), 29.

The number of equivalents of nitrous and nitric acid derived from the pentachlorethane were therefore 0.00607.

From nitric acid of the same strength when shaken with pentachlorethane, acid equivalent to 0.00062 was abstracted, due to the partition of the acid between the water and the pentachlorethane. The corrected figure for the former experiment was therefore 0.00545. Titration of the same solution with normal permanganate neutralized 6.12 cc. or 0.00612 equivalents.

To distinguish between nitrous acid from N_2O_3 and that from N_2O_4, recourse was made to the use of simultaneous equations.

Since

$$N_2O_3 + H_2O = 2HNO_2$$

$$N_2O_4 + H_2O = HNO_2 + HNO_3$$

it is evident that if x = number of molecules of N_2O_3 in the extract and y = number of molecules of N_2O_4 accompanying it, the total number of equivalents reacting with alkali is

$$2x + 2y = 0.00545.$$

But in the case of oxidation according to the equation

$$HNO_2 + O = HNO_3$$

the equivalent weight of HNO_2 in oxidation is one-half that when reacting as an acid. The total number of equivalents reacting with permanganate is therefore

$$4x + 2y = 0.00612.$$

Hence $2x = 0.00067$, or $x = 0.000335$ and $y = 0.00239$, whence $\frac{y}{x} = 7.13$.

The N_2O_3 has been derived entirely from the N_2O_4 since none was present at the start, and since 2 mols. N_2O_4 give one mol. N_2O_3, we can substitute in the place of it one-half the N_2O_4 converted.

We have therefore

$$7.13 = \frac{N_2O_4 \text{ remaining}}{{}^1/_2\, N_2O_4 \text{ converted}} = \frac{0.4425 — N_2O_4 \text{ (converted)}}{{}^1/_2\, N_2O_4 \text{ (converted)}}$$

whence N_2O_4 (converted) = 0.0972.

This has been converted into N_2O_3 and HNO_3 according to the equation

$$2N_2O_4 + H_2O = N_2O_3 + 2HNO_3$$

and has given rise to $0.0972 \times \frac{46}{184} = 0.0401$ g. N_2O_3 and $0.0972 \times \frac{126}{184} = 0.00666$ g. HNO_3, and the water remaining $= 0.0972 \times \frac{18}{184} = 0.0097$ g. H_2O.

In the original quantity of aqueous acid there were 4.0522 g. HNO_3 and 2.0628 g. of water, so that the weights in equilibrium are

$$\begin{aligned} HNO_3 &= 4.0522 + 0.0666 = 4.1188 \text{ g.} = 0.0654 \text{ mol.} \\ H_2O &= 2.8628 — 0.0097 = 2.8531 \text{ g.} = 0.1585 \text{ mol.} \\ N_2O_3 &= 0.0401 \qquad\qquad\qquad = 0.0529 \text{ mol.} \\ N_2O_4 &= 0.4425 — 0.0972 = 0.3453 \text{ g.} = 0.3755 \text{ mol.} \end{aligned}$$

$$\text{whence } K = \frac{3755^2 \times 1585}{529 \times 654^2} = 0.97.$$

The other values were calculated in a similar manner.

Attempts to measure the rate of reaction in 50 to 60 per cent nitric acid were without success as it is practically instantaneous even at —10° C.

From this value of K we may calculate the equilibrium concentrations of N_2O_4 and N_2O_3 in nitric acid of various strengths, and this permits us to obtain an approximation as to the amount of absorption of NO_2 which would occur on passage into nitric acid when secondary oxidation does not take place.[1]

THE PREPARATION OF STRONG NITRIC ACID

From the previous considerations the hypothesis was advanced that the limitation in the strength of acid produced by the interaction of nitrogen dioxide and water was due not to the volatility of nitrous acid or to its decomposition, but to the reducing action of nitrous anhydride on strong nitric acid,

$$N_2O_3 + 2HNO_3 = 2N_2O_4 + H_2O.$$

It therefore appeared possible that the equilibrium would be shifted over to the left with the production of strong acid provided that the continuous removal of N_2O_3 could be ensured without simultaneous removal of N_2O_4 or the addition of too much water. This could be effected by strictly limiting the amount of water vapor in the condensation of a mixture of N_2O_4, air and water vapor, and converting any dissolved nitrous anhydride into nitrogen dioxide by agitation with oxygen.

To test this point a gaseous mixture of NO_2 and oxygen in the proportion of four to one by volume, the oxygen being previously charged with sufficient water vapor to produce 100 per cent nitric acid on complete condensation, was passed directly into a cooling system consisting of a wide glass U-tube connected to a spiral condenser 9 ft. long, maintained at —5° C. The condensate obtained was observed to separate into two distinct layers on standing. Analysis of each layer gave the following results:

UPPER LAYER	Per cent	LOWER LAYER	Per cent
NO_2	50	NO_2	29.4
HNO_3	50[1]	HNO_3	43.4
H_2O	Trace	H_2O	27.2
Concentration of HNO_3 = 100		Concentration of HNO_3 = 61.5	

[1] The presence of a small quantity of N_2O_3 in the upper layer vitiated the accuracy of these figures.

It appears probable that the original condensate is acid of 60 to 65 per cent concentration which dissolves more nitrogen dioxide, the nitrogen trioxide produced being continuously re-oxidized by oxygen. The acid is raised to such a concentration by this method that the addition of a small excess of nitrogen dioxide causes the separation into two layers, owing to the difference in solubility of weak and strong nitric acid in liquid N_2O_4.

It has been previously shown by Fritzsche that strong nitric acid separated into two layers on the addition of liquid N_2O_4. Meister Lucius and Brüning[2] have shown that separation into two layers occurs only with acid of 80 per cent concentration and over, the upper layer consisting of 98 to 99 per cent nitric acid containing dissolved N_2O_4, and the lower layer of aqueous HNO_3 more dilute than that originally taken for treatment.

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[1] Partington and Parker, *Loc. cit.*

[2] British Patent 4,345 (1915).

The above experiment was repeated and the condensed layers treated with a slow stream of oxygen to remove all traces of the N_2O_3.

	Upper Layer Per cent		Lower Layer Per cent
NO_2	72.4	NO_2	11.0
HNO_2	25.7	HNO_3	74.3
H_2O	1.9	H_2O	14.7
Concentration of HNO_3 = 91.9		Concentration of HNO_3 = 84.0	

Having shown the applicability of this process to the direct preparation of strong nitric acid from nitrogen dioxide and oxygen, attempts were made to prepare strong nitric acid from a mixture of NO_2, air and oxygen. For this purpose oxygen was introduced along with the air supply and the concentration of NO_2 in the gas mixture was maintained at a low figure, approximating technical conditions of operation in denitrator towers, *viz.*, 20 per cent of the air content.

Air rate = 60 cc. per min. (at 30° C.) saturated with water vapor
Oxygen rate = 60 cc. per min. saturated with water vapor at 18° C.
NO_2 rate = 60 cc. per min. dry
Temperature of cooling spiral = —8° C.

Analysis of the Condensate

	Per cent
HNO_3	85.4
NO_2	6.1
H_2O	8.5

Concentration of nitric acid = 91.2

The conditions necessary to obtain concentrated acid from weaker gases, *e. g.*, those containing 10 to 13 per cent of NO_2 by volume, such as are obtained in ammonia oxidation processes, were next examined. From vapor pressure data the point of commencement of liquefaction of nitrogen dioxide of various concentrations has been determined as follows:

NO_2 in Gas Per cent	Commencement of Liquefaction of N_2O_4 ° C.
50	+8
25	—6
20	—12
15	—18
10	—23
5	—35
1	—60

It was at once evident that the direct condensation of dry dilute NO_2 required extremely low temperatures for operation. Provided, however, a more easily condensable constituent of the gas phase be present which is a solvent for nitrogen dioxide, the removal of NO_2 can be effected at the temperature of liquefaction of the solvent. In the present series of experiments this solvent was dilute nitric acid produced from the water vapor present in the gases.

The following method of procedure was adopted: A 12 per cent NO_2-air mixture obtained from a small platinum gauze ammonia oxidation converter was cooled quickly to 20° C. in order to separate out the excess of water, over and above that necessary for the completion of the equation

$$2N_2O_4 + 2H_2O + O_2 = 3HNO_3.$$

This gas was then led into cooling vessels immersed in freezing mixtures of ice and salt in order to condense out the nitric acid formed. With a flow rate of 1.5 liters of gas per min., a condensate of 61.2 per cent, increasing to 78.1 per cent acid strength at —10° C., was obtained.

SUMMARY

1—The rate of absorption of nitrogen dioxide by water and nitric acid solutions follows a monomolecular law. In aqueous solutions the reaction is pseudo-monomolecular, being a process of physical solution, the rate depending on the partial pressure of NO_2 in the gas phase. In strong acid solutions the reaction is a true chemical monomolecular reaction, the rate depending on the concentration of the N_2O_4. An inversion of the temperature coefficient of absorption occurs at 10 per cent nitric acid strength.

2—The limitation of acid produced in nitric acid absorption towers to concentrations of 64 per cent nitric acid is due to the reduction of nitric acid by nitrous anhydride produced in solution, according to the reversible equation

$$2HNO_3 + N_2O_3 \rightleftharpoons H_2O + 2N_2O_4.$$

The equilibrium constant of this equation at ordinary temperatures is approximately $K = 0.81$.

3—The production of nitric acid exceeding 64 per cent in strength is possible, provided that the N_2O_3 be continuously converted into nitrogen dioxide by agitation with oxygen.

4—The production of strong nitric acid may be accomplished by a process of refrigeration of a gas mixture containing suitable proportions of nitrogen dioxide, water vapor, and oxygen.

THE PRODUCTION OF HYDROCHLORIC ACID FROM CHLORINE AND WATER

By H. D. Gibbs

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Received October 28, 1919

Since the utilization of the potentially large production of chlorine brought about through war requirements offers some difficulties, pending the establishment of an equilibrium by adjustment of the chemical industries from a war to a peace basis, the economic conversion of chlorine into hydrochloric acid has been investigated.

Early in the study of elementary chemistry one learns that chlorine reacts with water in the sense of the expression

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

and that the hypochlorous acid decomposes thus,

$$HClO \longrightarrow HCl + O.$$

Owing to the instability of hypochlorous acid in the presence of hydrochloric acid, the first reaction progresses to a very limited extent and the production of the end-products, oxygen and hydrochloric acid, is greatly accelerated by light. This accounts for the fact that aqueous solutions of chlorine eventually become aqueous solutions of hydrochloric acid upon standing in the laboratory, and should therefore be protected from the light. A catalyst that will speed these reactions and afford a cheap method of conversion of chlorine and water into hydrochloric acid and oxygen could be made the basis of a valuable commercial process.

This is the reversal of the Deacon process. The catalyst for the Deacon process is usually described as a rough surface impregnated with cupric chloride, although many other substances, such as the chlorides of iron, nickel, cerium, or alunite[1] may be employed. Lewis[2] has described a careful investigation of the equilibrium of the Deacon process, employing the first of these catalysts, and it is evident that the reversal, producing hydrochloric acid and water, is best carried out at high temperatures. The equilibrium constant

$$K = \frac{p^{1/2\,Cl_2}\ p^{1/2\,H_2O}}{p^{\,HCl}\ p^{\,1/4 O_2}}$$

decreases from 4.15 at 352° C. to 2.40 at 419° C. as shown from his experimental work, and to 0.133 at 1537° C. as calculated.

A catalyst which will produce the desired products, hydrochloric acid and oxygen, to a satisfactory degree has not as yet been developed. This paper merely describes the present state of the work when charcoal is employed as a catalyst.

HYDROCHLORIC ACID FORMED BY THE UNION OF HYDROGEN AND CHLORINE

Processes have been devised for converting chlorine into hydrochloric acid by union with hydrogen. A process at low temperature was patented by Pataky[3] who states that the combination of hydrogen and chlorine may be effected in a quiet and continuous manner by passing the gases in molecular proportion over coarsely pulverized charcoal, controlling the temperature by means of a water bath. Conroy[4] in commenting upon Pataky's process for getting rid of an excess of chlorine states:

> The process is intended as an adjunct to the manufacture of chlorine and alkali by electrolysis, but it is far from likely that it will ever come into extended use.

Garner and Clayton[5] obtained a patent on the manufacture of hydrochloric acid by the union of dry chlorine and dry hydrochloric acid in presence of wood charcoal at temperatures above 340° C., and they also provide a slight modification in the procedure to be employed if moisture is present. They state:

> As hereinbefore indicated, the gases can advantageously be dried before their admission into the chamber containing the catalyzer, for the reason that if moisture is present the reaction proceeds too violently when equal volumes of hydrogen and chlorine are used. We have discovered, however, that the reaction will still proceed smoothly and without explosive violence even though moisture is present, provided the hydrogen is used in excess, such as 50 parts of hydrogen by volume to 35 parts of chlorine by volume, or by using any larger excess of hydrogen. In fact, under such conditions, the temperature required for the reaction is about 340° C.

There are three claims, the first being:

> The method of making hydrochloric acid which comprises causing hydrogen and chlorine to react at a temperature of not below about 340° C. in the presence of wood charcoal, moisture being present in the reacting gases and the hydrogen being employed in excess, and recovering the hydrochloric acid thus formed, substantially as described.

These patents differ from each other essentially in the factor of temperature.

An excess of chlorine has recently been taken care of in at least one plant by combustion with hydrogen at high temperature. The heat was removed by water cooling the combustion apparatus.

HYDROCHLORIC ACID FORMED BY THE REACTION BETWEEN CHLORINE AND WATER

During the investigation in this laboratory[1] of the absorption of chlorine by various kinds of charcoal, it was found that the moisture content of the gases coming in contact with the charcoal at room temperature greatly influenced not only the rate of absorption but also the nature of the phenomenon. There are other important factors that will be discussed later in this paper. When the chlorine-air mixture is dry the chlorine is removed from the air and is retained by the charcoal, while with moist gases a chemical change takes place that is manifested by a reaction between the water and the chlorine in the sense of the equation

$$2Cl_2 + 2H_2O + C = 4HCl + CO_2.$$

The reaction is very satisfactory in that all of the chlorine may be converted into hydrochloric acid but very disappointing in that the oxygen does not appear as such, but, as might be predicted, unites with the carbon. The formation of hydrochloric acid has been found to proceed over a very wide temperature range above 80° C., preferably between 80° and 200°, and large quantities of chlorine can be handled in a comparatively small apparatus.[2]

The best procedure is to blow the steam and chlorine through a large bed of charcoal of the character used for absorbing gases—coconut charcoal, ivory nut charcoal, and other varieties especially treated—and at the same time small quantities of air may be admitted to assist in sweeping out the products of the reaction. The process is highly exothermic and the excess of water and air carries off the heat generated in the catalytic mass.

After this process was developed on a laboratory scale it was found that it had been partially described in the literature and that two investigators had patented the process at two different temperature ranges above 100°. Lorenz[3] states:

> In many technical processes, such as in the electrolytic production of metals from their chlorides, chlorine is produced as a by-product.
>
> In most cases, however, it is not possible to render the chlorine thus produced commercially available.
>
> It is therefore desirable to convert such chlorine into a commercially valuable compound.
>
> According to my present invention I effect this in converting the chlorine into hydrochloric acid by passing it together with steam through a clay retort filled with coke, charcoal, or anthracite, and heated to a low red heat. By this means chemically pure hydrochloric acid is obtained.
>
> I have found that in the same manner bromine can be converted into hydrobromic acid, namely, by passing vapors of bromine together with steam through a clay retort filled with

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[1] U S. Patent 1,311,175 (1919).

[2] *J. Am. Chem. Soc.*, **28** (1906), 1380.

[3] D. R. P., 114,219 (1899); Brit. Patent 1,831 (1900).

[4] *J. Soc Chem Ind*, **21** (1902), 304.

[5] U. S. Patent 1,220, 411 (1917), assigned to Metals Research Company of New York, N. Y.

[1] G. S. Bohart and E. Q. Adams, "Some Aspects of the Behavior of Charcoal with Respect to Chlorine," *J Am. Chem. Soc.*, **42** (1920), 523. I am indebted to them for much data and the curves.

[2] U. S. Patent pending.

[3] Brit. Patent 25,073 (1894).

> coke, charcoal, anthracite or the like, and heating to a low red heat.
>
> The production of hydrochloric acid from chlorine and of hydrobromic acid from bromine by passing the chlorine or bromine together with steam through vessels filled with coke, charcoal, or anthracite heated to a low red heat, the resulting hydrochloric acid or hydrobromic acid being then separated from the other resulting gases by condensation substantially as described.

Peter[1] states:

> According to the process of this invention, hydrochloric acid is produced from chlorine by means of water-vapor. I believe that I am the first to discover that by properly proportioning the chlorine and water-vapor, hydrochloric acid can be produced at low temperature and the first to provide means by which the proper proportioning may be determined and accomplished.
>
> In carrying out the process of the present invention, the chlorine in contact with water or water-vapor forms hydrochloric acid and liberates oxygen, and in order to accelerate the latter reaction it is desirable to have present a substance or substances to take hold of the oxygen, as, for example, carbon or sulfur, and I prefer to use carbon in the form of charcoal or coke.
>
> By the process of the present invention, the chlorine may be converted quantitatively into hydrochloric acid at a temperature as low as 200° C. and the chlorine may be converted into hydrochloric acid at temperatures just above boiling point of water.

There are seven claims in the patent, the broadest being: "A process for making hydrochloric acid comprising the conversion of chlorine into hydrochloric acid by means of water-vapor and carbon at a temperature lower than red heat."

Other claims fix the temperature range "between the boiling point of water and red heat" although there is nothing to show that the inventor considered the patent operative below 200°.

It is to be noted that the only difference of any importance in these patents is the reaction temperature.

In regard to the mechanism of the reaction, Lorenz[2] points out that it has been known for many years that chlorine and water do not react in the dark at low temperatures, unless there be present some substance to react with the oxygen, such as boron, phosphorus, sulfur, selenium, iodine, phosphorous acid, sulfurous acid, or an oxidizable carbon compound. He states that the reaction goes quantitatively according to the equation

$$2Cl + H_2O + C = 2HCl + CO.$$

Naumann and Mudford,[3] and Naumann[4] point out that the reaction

$$2H_2O + C = CO_2 + 2H_2$$

goes on below 600° C. and that the reaction between chlorine, water, and carbon should be expressed

$$2Cl_2 + 2H_2O + C = 4HCl + CO_2,$$

and that any carbon monoxide formed arises from the decomposition of the carbon dioxide in presence of carbon. Moreover, any carbon monoxide formed will be oxidized according to the equation

$$Cl_2 + H_2O + CO = 2HCl + CO_2.$$

They show that at higher temperatures, above 400° C., an excess of water-vapor results in formation of carbon dioxide, carbon monoxide, and hydrogen. The thermal relations of the various reactions involved are discussed and the conclusion is reached that, since the balance is highly exothermic, a valuable process might be evolved.

It is possible that the catalytic action of the charcoal is of greater importance than indicated in the above work and that the reaction between water and chlorine is catalyzed by the charcoal in the sense of the equation

$$Cl_2 + H_2O = 2HCl + O,$$

the active oxygen liberated disappearing simultaneously through union with the carbon. The fact that the reaction has a very appreciable speed at room temperature, and even as low as 0°, offers some support of this theory. The necessary energy is supplied to the reaction by the combustion of the charcoal.

INFLUENCE OF TEMPERATURE—The four curves of Fig. 1 show the effect of temperature at four different ranges, 0°, 12°, 25°, and 37.5°, upon the amount of the chlorine converted into hydrochloric acid, all other conditions being constant.

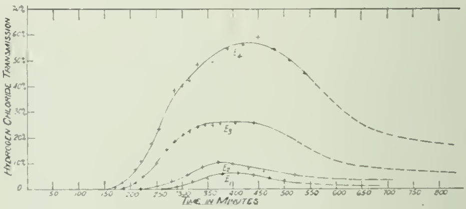

FIG. 1—THE PRODUCTION OF HYDROGEN CHLORIDE AT FOUR DIFFERENT TEMPERATURES

CONSTANTS: Catalyst, Charcoal E; depth of layer, 10 cm.; cross section, 10.75 cm^2.; weight, 67 g.; mesh, 8 to 10 per in.; velocity of gas, 500 cm. per min.; air-chlorine ratio, 500 to 1; water content of air, 50 per cent saturation; pressure of gas above charcoal, 1 atmosphere; pressure of gas below charcoal, 1 atmosphere minus 0.85 cm. water

VARIABLES: Temperature. Curve E_1, 0.0°; E_2, 12.0°; E_3, 25.0°; E_4, 37.5°

The investigation at higher temperatures is now being carried on. By maintaining a slight reduction in pressure upon the charcoal, the reaction between water and chlorine is being studied in the vapor phase below 100°. The indications so far obtained are that, under these conditions with the water-vapor greatly in excess of the requirements, the chlorine can be completely converted to hydrogen chloride over long periods of time without changing the bed of charcoal catalyst and that the curve of production, after the initial rise, gradually falls off to a point where it remains comparatively flat.

INFLUENCE OF AMOUNT OF WATER—It is evident that an excess of water over that necessary to react with the chlorine is desirable. In Fig. 2 the curves of hydrogen chloride production are plotted for different moisture content of air, namely, 0, 20, 40, and 80 per cent saturation. The curves showing the amounts of chlorine escaping unaltered at the same time are also shown.

It is to be noted that curve F_1 shows some production of hydrogen chloride with dry air. This is due to the fact that it was not found practicable to remove all moisture from the charcoal except by the progress of

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[1] U. S. Patent 1,229,509 (1917), assigned to Royal Baking Powder Company of New York, N. Y.

[2] *Z. anorg. Chem.*, **10** (1895), 74.

[3] *Ber.*, **30** (1897), 347.

[4] *Z. angew. Chem.*, **1897**, 197.

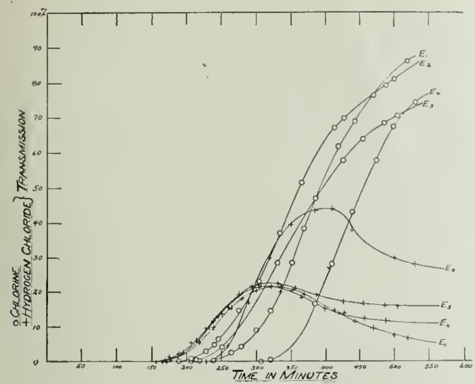

FIG. 2—CURVES SHOWING THE PRODUCTION OF HYDROGEN CHLORIDE (MARKED +) AND AMOUNT OF CHLORINE (MARKED O) ESCAPING ACTION WHEN VARYING AMOUNTS OF WATER ARE PRESENT

CONSTANTS: Charcoal E; depth of layer, 10 cm.; cross section, 10 75 cm².; weight of charcoal, 67 g.; mesh, 8 to 10 per in.; temperature, 25°; velocity of gas, 500 cm. per minute; air-chlorine ratio, 500 to 1; pressure of gas above charcoal, 1 atmosphere

VARIABLES: Water content of air, E_1, 0; E_2, 20; E_3, 40; and E_4, 80 per cent saturation

The molar ratios of water to chlorine are, 0:1: 3.1: 1: 6.2:1; 12.4·1

the reaction itself. The really significant parts of these curves are the ones indicating that the production of hydrogen chloride is in each case reaching a constant rate dependent upon the amount of water present. Later experiments conducted without air and with the water-vapor greatly in excess of the requirements of the reaction indicate that large-scale production of hydrochloric acid is possible by this method.

CATALYTIC VALUE OF DIFFERENT CHARCOALS—It is well known that different charcoals, and charcoals treated by different processes, have greatly varying powers of absorbing gases, and other substances such as dyes, colors, and impurities from solutions. It is also evident from the work of Bohart and Adams[1] that different charcoals show great differences in the catalysis of the reaction between chlorine and water. As an illustration of this fact the curve E_3, Fig. 1, may be compared with the hydrogen chloride curve of Fig. 3.

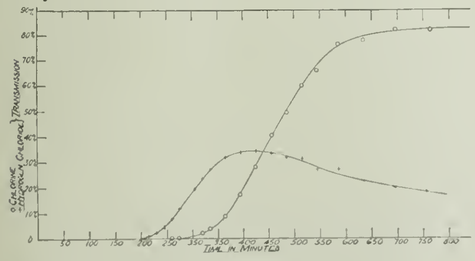

FIG. 3—CURVES SHOWING THE PRODUCTION OF HYDROGEN CHLORIDE (MARKED +) AND AMOUNT OF CHLORINE (MARKED O)

CONSTANTS: Charcoal F; depth of layer, 10 cm.; cross section, 10.75 cm².; weight of charcoal, 65 g.; mesh, 8 to 10 per in.; temperature, 25°; velocity of gas, 500 cm. per min ; air-chlorine ratio, 500 to 1; pressure of gas above charcoal, 1 atmosphere; pressure of gas below charcoal, 1 atmosphere minus 0.97 cm. of water; molar ratio of water to chlorine 7.7: 1

The conditions of the experiments were identical in every respect except that the charcoals were different. Charcoal F shows a maximum hydrogen chloride production of 34 per cent, while Charcoal E reaches 26 per cent. The curves fall off at the end of 800 min. to 18 per cent in the case of F, and 7 per cent in the case of E. Other charcoals are known to show even greater differences at low temperatures. Accurate comparisons are not available at higher temperatures.

It is to be noted in Figs. 1, 2, and 3 that the delay in the appearance of hydrogen chloride is due to the absorptive action of the charcoal on this gas and not to any induction period in the reaction.

SUMMARY

1—It is shown that the reaction between chlorine, water, and charcoal between 0° and about 130° C. produces hydrogen chloride and carbon dioxide, and that the most important factors influencing the speed of the reaction are the character of the charcoal, the temperature, and the relation between the concentrations of the water and the chlorine.

2—A reversal of Deacon's process is discussed and it is interesting to note that changing industrial conditions have made it of possible commercial application.

THE CORROSION OF BRASS IN DILUTE ELECTROLYTES[1]

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Received January 21, 1920

The corrosion of metals and alloys is conditioned by a number of influences, such as the composition of the metal, the dissolved substances present in the liquid in contact with it, temperature, stirring, dissolved oxygen, homogeneity, contact with metals and catalytic agents, the previous mechanical and thermal treatment of the metal, the nature of its surface, and so forth. In view of this large number of influences which are operative in the process of corrosion, and especially inasmuch as some of them are decidedly indefinite and hard to control, it is not surprising that the results and theories of corrosion are as diverse and conflicting as the literature shows them to be. The principle of studying each influence individually seems the most promising method of attack for this problem, and has been used in the present work.

A large amount of valuable work has been done on this problem, and the authors have freely availed themselves of the information already in the literature. Very noteworthy in this respect are the elaborate researches of Bengough and his collaborators[1] on the corrosion of brass condenser tubes by sea water. These investigators, however, have considered the influence of the components of the solution *en masse*, and have given no attention to the individual behavior of each of the various ingredients. In the work of the Illinois State Water Survey, it has been found that certain waters are very corrosive to the brass working parts of water meters and pumps. It was this fact which suggested the present investigation and led the writers to limit their experimental work to such ions as ordinarily occur in natural waters.

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[1] *Loc. cit.*

[1] This article is published as a more or less preliminary report. The writers are fully aware that certain phases of the problem have been only superficially investigated, and others have been omitted altogether. It is planned to continue this study at a later time.

The Fourth Report of the Corrosion Committee of the Institute of Metals, written by Bengough and Hudson (*J. Inst. Metals*, **21** (1919), 37), was received after the experimental work of this paper was finished It appears that part of the work of these investigators has been duplicated in our work and the conclusions that have been reached on certain points are identical. However, it has been deemed best to publish our paper in its original form, not only as a substantiation of the results of the above investigators, but particularly to present a unified account of our work which contains a large amount of experiment and inference not covered in the British paper.

Bengough has defined two types of corrosion,[2] "complete" and "selective." In "complete" corrosion the components of the brass are equally corroded—that is, in the proportion in which they occur in the alloy. This form of corrosion is due to direct oxidation by dissolved oxygen. In "selective" corrosion only one ingredient (the zinc) is corroded. The action is electrochemical and depends on differences of potential, either within the brass itself, or between the brass and some metal in contact with it.

SELECTIVE OR ELECTROLYTIC CORROSION

It is generally accepted that any set of conditions that will bring about a difference of electric potential between two metals in metallic connection, or between the components of an alloy, will result in electric currents, and corrosion will take place at the expense of the metal of highest solution pressure. In the case of brass, the corroded element is usually the zinc, and its removal is called "dezincification." The characteristic of this selective form of corrosion is pitting, or in the more serious cases, perforation. The zinc is removed, leaving the copper matrix in a porous and weak form. The action is localized around that part of the couple which functions as the cathode, and in general appearance it differs conspicuously from corrosion due to oxidation.

In order to study the part that the various ions of a solution may play in electrolytic corrosion, the writers have carried out the following experimental work.

MAGNITUDE OF POTENTIAL DIFFERENCES—The potential differences between pieces of bright copper and bright zinc were measured at room temperature (21° to 22° C.) in several solutions, obtaining initial values of 0.9–1.0 volt (Table I). Assuming that there are discrete particles of copper and zinc present on the surface of the brass, this gives an approximate measure of the intensity factor operating at the start in the electrolytic corrosion of brass. This difference becomes smaller as corrosion proceeds, due to polarization effects, but since in practice the volume of the solution is exceedingly large and since the liquid is frequently in constant motion, the working value of this potential may remain high. This was shown in the following manner: The electrodes just referred to were short-circuited for 24 hrs. in a 0.1 *M* potassium chloride solution, washed as thoroughly as possible in that solution, and upon remeasuring gave a potential of 0.76 volt. This indicates that, with an electrolyte of good conductivity, electrolytic corrosion of brass may be very considerable.

TABLE I—POTENTIAL DIFFERENCES BETWEEN COPPER AND ZINC

	Volts
Cu : 0.1 *M* HCl : Zn	0.92
Cu : 0.1 *M* KCl : Zn	0.92
Cu : 0.1 *M* KNO_3 : Zn	0.92
Cu : 0.1 *M* KNO_2 : Zn	0.98
Cu : 0.1 *M* NH_4Cl : Zn	0.95
Cu : 0.1 *M* $NaHCO_3$: Zn	1.04

ROLE OF THE IONS—The corrosive influence of the common ions of natural waters was investigated by means of current-potential curves. An electrolytic cell was set up, using as an anode a piece of 80 : 20 brass, 2 × 2.5 cm., and as a cathode a piece of bright sheet platinum. Care was taken that the relative positions of the electrodes should be unchanged in the various experiments, and that the stirring should be as uniform as possible. Fig. 1 shows a diagrammatic arrangement of the apparatus. Increasing potentials were applied by means of the sliding resistance R, and were read directly from the voltmeter V, which was placed on a shunt around the cell and the milliammeter M.

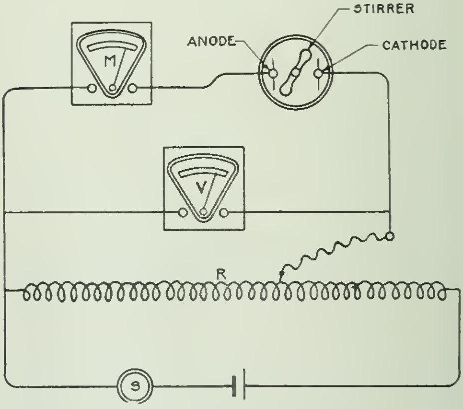

FIG. 1—DIAGRAM OF APPARATUS

The curves for 0.1 molar solutions of potassium nitrate, chloride, and bicarbonate are shown in Fig. 2. The curves for 0.05 *M* K_2SO_4 and 0.1 *M* KNO_2 are almost superposable with that for 0.1 *M* KNO_3, and for that reason were not included in the figure. On account of the double flexure in the potassium chloride curve it is not easy to compare the influences of these anions on corrosion. Assuming that the operative potential lies within the range 0.7 to 1.0 volt, it would appear that there is very little difference in the corrosive effects of Cl, NO_3, NO_2, and SO_4 ions. The action of HCO_3 ion is, for some unexplained cause, much less than the others.

The sinuous form of the chloride curves requires an explanation. All the chloride solutions used showed decided double flexures, with the exceptions of hydrochloric acid and ammonium chloride. The double flexure in current-potential curves is generally interpreted to mean a change in reaction at one of the electrodes. In the case of solutions containing Cl^- ions, the anode reaction with brass electrodes at low potentials seems to be the discharge of Cl ions, forming cuprous chloride as a primary product. Owing to the insolubility of cuprous chloride, polarization effects are very slight, and the current mounts rapidly with the first increase in potential. At higher potentials a second reaction begins—the direct ionization of the copper of the brass—and this gives a second stimulus to the current. The second flexure is in the neighborhood of a potential of 1.0 volt, its position being displaced in different solutions by different cathode potentials. In some cases, as for instance hydrochloric acid and ammonium chloride, curves of apparently different types were obtained, but the abnormality is more apparent than real. In hydrochloric acid the second flexure is displaced to the left by an elevation of the cathode potential, and in ammonium chloride the first part of the curve is modified by a side reaction—the formation of NH_3 complexes.

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[1] *J. Inst. Metals*, **10** (1913), 13; **15** (1916), 37.

[2] *Ibid.*, **10** (1913), 21.

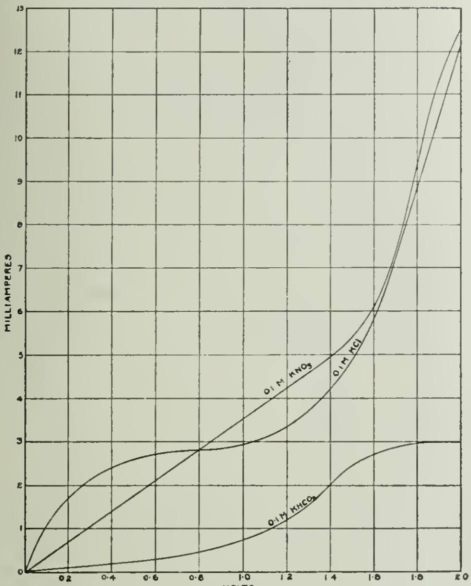

FIG. 2—INFLUENCE OF ANIONS IN ELECTROLYTIC CORROSION

Current-potential curves were taken for sets of solutions having a common anion, so as to get comparative values for the influence of several cations (Fig. 3). With hydrochloric acid solution marked corrosion is indicated, as would be expected from the high mobility of the hydrogen ion. With solutions of metallic chlorides, the corrosion is much less. This is due to the fact that the cathode reaction is the discharge of hydrogen ions, and the amount of current passing at the cathode depends directly upon the concentration of these ions. From this it follows that solutions which are acid, either by reason of a free acid or owing to hydrolysis, are favorable mediums for corrosion. Ammonium and calcium chloride solutions appear more corrosive than potassium and sodium chlorides of equivalent concentration, the difference being due to the hydrolytic formation of free hydrochloric acid in the first two solutions.

Fig. 4 shows the effect of concentration on electrolytic corrosion. It is significant that the current increases with the conductance of the solution, indicating that in electrolytic corrosion high concentrations, by lowering the resistance of the liquid part of the circuit, would strongly stimulate corrosion.

It has been suggested by some writers[1] that a solution containing two or more salts might be more corrosive than the combined effect of the component salts when taken separately. Current-potential curves were taken for several mixtures, and the total current was found to be very nearly equal to the sum of the currents for separate solutions of single salts of equivalent concentrations to those in which they occurred in the mixture. It is inferred that the influence of the various ions on electrolytic corrosion is an additive property.

CORROSION PRODUCTS—Very naturally corrosion products vary with the electrolyte. The products for low potentials in neutral solutions are basic salts, only loosely adherent to the anode. At higher potentials the solution becomes turbid and its color shows an increasing amount of dissolved copper. Basic copper chloride was found to be very stable, and constituted the principal part of the corrosion product with neutral chlorides. With nitrates and sulfates, basic zinc salts seemed to predominate. Solutions containing HCO_3 ions appeared rather non-corrosive from the electrolytic point of view, and no appreciable precipitate formed unless high potentials were used.

INFLUENCE OF DISSOLVED OXYGEN IN ELECTROLYTIC CORROSION—Some have assumed that dissolved oxygen would stimulate electrolytic corrosion by acting as a depolarizer at the cathode. In order to verify this assumption, current-potential curves were taken for 0.1 *M* KNO_3, using a brass anode and a copper cathode. In one experiment, the solution (previously boiled to expel air) was stirred by a jet of nitrogen bubbled into the solution close to the cathode. In a second run, the solution was stirred with filtered CO_2-free air instead of nitrogen. The curves were identical within the limits of experimental error. A solution of 0.1 *M* KCl gave similar results. It is therefore concluded that dissolved oxygen is without significant effect in electrolytic corrosion.

COMPOSITION OF THE BRASS—The measurements cited above were made with an anode of commercial brass containing 80 per cent copper and 20 per cent zinc. Other brasses ranging from 90: 10 to 60: 40 gave potential measurements of the same order as those with the 80 : 20 form. The results given here are merely representative. The specific effects of variation in composition of the brass will be studied further.

INFLUENCE OF TEMPERATURE—At elevated temperatures the effects of electrolytic corrosion are greater[2], and the life of brasses exposed to aërated natural waters is much shortened, owing to pitting and possible perforation. High temperatures favor corrosion in two ways, *viz.:*

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[1] Gaines, *Eng. News*, **59** (1908), 578; Heyn and Bauer, *Mitt. kgl. Materialprüfungsamt*, **28** (1910), 62.

[2] Bengough and Jones, *J. Inst. Metals*, **10** (1913), 50.

1—The mobility of the ions is increased, thus greatly reducing the resistance of the liquid phase of the circuit.

2—There is an acceleration in the speed of the reactions involved, such as the ionization of the zinc, and so forth.

The above experiments suggest very strongly that, so far as electrolytic corrosion is concerned, the role of most ions is immaterial, except as they maintain the conductivity of the solution. Certain ions, on the other hand, show a specific corrosive action. In the case of chlorine ions, this is connected with the removal of the ions of the anode metal by converting them into insoluble compounds or into complexes of low ionization. In other words, they act as depolarizers.

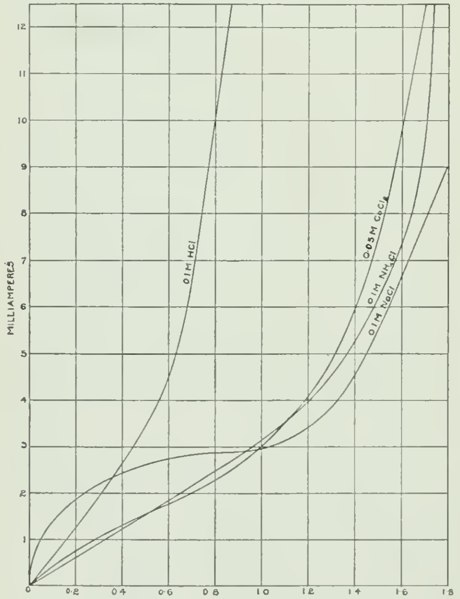

FIG. 3—INFLUENCE OF CATIONS IN ELECTROLYTIC CORROSION

As another example, waters containing hydrogen sulfide are corrosive to brasses, not so much on account of their acidity as the formation of insoluble zinc sulfide and copper sulfide. Solutions of ammonium salts act very much in the same way, in that the solution becomes alkaline and free ammonia is formed, which unites with Zn and Cu ions to form NH_3 complexes of low ionization. This explains to some extent the large current with ammonium chloride solution.

COMPLETE CORROSION

It is easily demonstrated that fine copper is tarnished in the presence of moist air. Pure zinc is similarly coated with a layer of zinc oxide. Under similar conditions brass corrodes, but much more slowly, to a product containing copper oxide. It is clear that such reactions are not electrolytic, since in the first two cases the metals are quite homogeneous and the corrosion is general, not local. In the case of brass, electrolytic corrosion would hardly result in the solution of the nobler component. It appears that this form of corrosion is due to oxidation by dissolved oxygen, known as "complete" or "general" corrosion.

OXYGEN ESSENTIAL TO COMPLETE CORROSION—In corrosion hydrogen must be liberated, or oxygen (or some chemically analogous substance) must be taken up from the air or other oxidizing agent. In order to learn whether hydrogen was liberated, pieces of soft brass, 1.5 × 7 cm., were placed in 0.1 *M* solutions of HCl, KCl, NH_4Cl and NH_4NO_3, each of which had been boiled to expel absorbed oxygen. The apparatus consisted of 20 cc. glass-stoppered weighing bottles, each of which, after introduction of the brass, was completely filled with the solution so as to exclude all bubbles. The bottle was placed in a cylinder and covered with an excess of the same solution to seal it from access of air by leakage. After standing for varying lengths of time (Table II), the brass remained bright and no bubbles of gas appeared in any of the tubes, indicating that no hydrogen was evolved. With 6 *M* HCl (sp. gr. 1.12) brass was likewise inactive at ordinary temperatures, but upon heating evolution of hydrogen began at temperatures slightly below 50°. Table II shows that, while there was no visible liberation of gas, there was a certain amount of corrosion in all cases, the amount, however, being small in comparison with that occurring when air was present.

TABLE II—EFFECT OF ABSENCE OF DISSOLVED OXYGEN ON COMPLETE CORROSION

SOLUTION	Dissolved Air	Length of Test Days	Loss in Weight Grams
0.1 *M* KCl	Saturated by frequent shaking	37	0.0125
0.1 *M* KCl	None	37	0.0010
0.1 *M* HCl	None	26	0.0012
0.1 *M* NH_4Cl	None	26	0.0003
0.1 *M* NH_4NO_3	None	24	0.0006
6 *M* HCl	None	17	0.0010

Hence it is concluded that oxygen is necessary to extensive corrosion of brass in dilute solutions at ordinary temperatures. Similar results were obtained by Adie[1] in his studies of iron, and have since been fully confirmed by the very careful investigations of Friend.[2]

MEASURE OF CORROSION—The usual procedure in determining the amount of corrosion has been to remove the corrosion product by some mechanical means, such as carefully polishing with an abrasive, or rubbing with a brush or rubber-tipped rod, and determining the corrosion by loss in weight. In the present work it has been found far quicker and more accurate to remove the deposit chemically. The corroded test piece is immersed in cold hydrochloric acid (sp. gr. 1.12) for one minute, rinsed thoroughly with distilled water which has been boiled to expel dissolved air, and dried between filter papers. In a series of four blank tests, using brass pieces 2.5 × 6.5 cm., the average loss on this treatment was 0.00035 gram. Ammoniacal and alkaline cyanide solutions were tried as solvents for the corrosion products, but discarded because of poor efficiency and a marked tendency toward oxide formation in the subsequent rinsing.

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[1] *Min. Proc. Inst. Civil Eng.*, **4** (1845), 323.

[2] "Corrosion of Iron and Steel," **1911**, 142

A very promising means of determining corrodibility of brass depends upon considering the oxygen consumed an index of corrosion. Pieces of brass of convenient size are placed in small tubes connected with mercury manometers of the open-arm type. The solution to be used is shaken with air at room temperature until saturated, and a definite volume introduced. The tube is best closed by sealing off the capillary end of a vent tube, so as not to disturb the level of the mercury in the manometer. This method affords a very convenient means of learning not only the relative corrodibility of two or more specimens of brass, but gives the necessary information about the speeds of corrosion. The use of rubber stoppers in this work is not recommended, since in most of the experiments where they were used the results were vitiated by leakage around the tubes or diffusion through the rubber. Ground glass joints seem to be required.

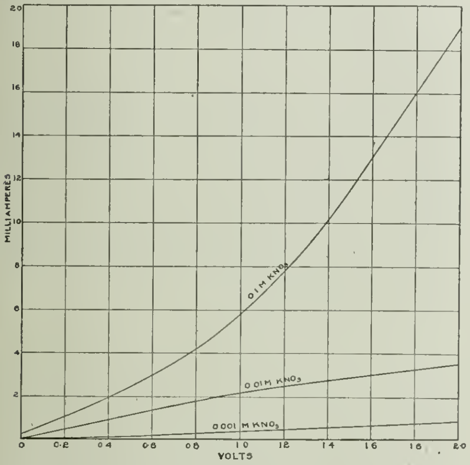

Fig. 4—Influence of Concentration on Electrolytic Corrosion

INFLUENCE OF IONS ON COMPLETE CORROSION—Many observers have reported that there are wide differences in the corrosive action of various solutions. To determine the specific influence of various solutions, pieces of soft brass, 2.5 × 6.5 cm., were placed in 150 cc. glass-stoppered bottles and covered with 100 cc. of the solution to be investigated. The bottles were thoroughly shaken so as to saturate the solutions with air, and the shaking was repeated every 24 hrs. These tests were carried out in groups of 18, and every care was taken to make the conditions as uniform as possible. After standing 15 days, the pieces were cleaned in hydrochloric acid of 1.12 specific gravity as described above, and the loss in weight determined. Table III gives the results obtained.

Comparative values of the influence of various anions may be obtained from a consideration of the 0.1 *M* potassium salts in the above table. They fall into the following order (the most corrosive first): HCO_3, Cl, SO_4, NO_3, NO_2, OH. The order of the cations is: H, NH_4, Mg, Ca, K, Na.

Table III—Comparison of Complete Corrosion in Various Solutions

Solution	Loss in Wt. Grams	Remarks
Distilled H_2O	0.0016	Brownish red tarnish
0.1 *M* HCl	0.0744	No stain. Cu-plate on edge
0.1 *M* KCl	0.0105	Local red stains. Slight precipitate containing Zn, Cu
0.1 *M* NaCl	0.0033	Local red stains. Slight precipitate containing Zn, Cu
0.1 *M* NH_4Cl	0.0721	No tarnish. Colorless solution. Blue precipitate containing Cu only
0.05 *M* $CaCl_2$	0.0151	Slight reddish stain. Precipitate containing Zn, Cu
0.05 *M* $MgCl_2$	0.0166	Slight reddish stain. Precipitate containing Zn, Cu
0.1 *M* KNO_3	0.0032	Local black splotches. Traces of NH_4 and NO_2 ions in solution
0.05 *M* K_2SO_4	0.0044	General tarnish. Local black stains. Trace of sulfide in corrosion product
0.1 *M* KNO_2	0.0017	Local black stains
0.1 *M* NH_4NO_3	0.1120	General black tarnish. Colorless solution. Precipitate containing Cu, Zn
0.1 *M* $NaHCO_3$	0.0155	General darkening, with local red stains
0.1 *M* $KHCO_3$	0.0249	General darkening, with local red stains
1.0 *M* KCl	0.0058	Bright. Slight precipitate containing Cu
0.01 *M* KCl	0.0092	Covered with red-brown stain
1.0 *M* NH_4Cl	0.3306	Bright. Blue solution. Green precipitate containing Cu
0.01 *M* NH_4Cl	0.0294	Red-brown stain. Blue solution. Greenish precipitate containing Cu, Zn

The HCO_3 ions were the first to show visible action. In from 5 to 6 hrs. the test pieces were almost wholly covered with a black deposit of what seemed to be copper oxide containing carbonates. The deposit seemed to exert little protection for the uncorroded brass, as is indicated by the high corrosion.

Marked corrosion has always been noted in solutions containing chlorides. Their specific action seems to be directly related to:

(1) The insolubility of the basic chlorides of zinc and copper.

(2) Their marked power for dissolving oxygen.

A characteristic of the corrosion by neutral chlorides is the formation of brownish splotches which appear to be regions of pure copper, and not of cuprous oxide, as some workers have reported. This conclusion is based upon the insolubility of these stains in dilute hydrochloric acid and potassium cyanide solutions. Another interesting observation, made only in chloride solutions, is the apparent copper plating of the brass. The deposit has exactly the same appearance as that formed upon placing brass in a solution of cupric chloride. It is suggested that the copper first goes into solution by general corrosion, and is later precipitated by the zinc of the brass.

Sulfates are characterized by a general darkening of the brass, and later by the formation of dark splotches. On the fourth day a slight precipitate of what was taken to be basic zinc sulfate appeared. A trace of CuS was formed during the corrosion, though the amount seemed too small to account for the total corrosion loss. It is thought that the main action is direct oxidation, rather than the reduction of sulfate to sulfide.

In nitrate solutions brass might be expected to behave as a zinc-copper couple, reducing the nitrate readily to ammonia. Here, as in other respects, there is a sharp contrast between brass and its constituents in the form of a couple. In the 0.1 *M* KNO_3 solution the brass piece seemed almost inert. With the exception of dark stains localized on some scorings formed in rolling the brass, the piece remained bright. At the end of the 15-day period of corrosion, Nessler's reagent and α-naphthylamine-sulfanilic acid reagent showed the presence of small amounts of ammonium and nitrite ions, respectively. Nitrites are even less corrosive than nitrates.

The corrosive influence of the cations has already been forecasted. The action of free acids—that is, of solutions containing the hydrogen ion—consists in dissolving oxides as fast as they form. Again, if the free acid has a specific oxidizing influence, like nitric acid, its corrosive effect will be accordingly intensified. Formation of free acids hydrolytically, as hydrochloric acid from magnesium chloride or nitric acid from ammonium nitrate, explains the marked increase of the corrosive action of these solutions over that of potassium chloride or nitrate. The ammonium group has an exceedingly corrosive effect by reason of the formation of NH_3 complexes. Tests with litmus paper showed a development of alkalinity in all the neutral salt solutions used.

INFLUENCE OF DISSOLVED OXYGEN ON COMPLETE CORROSION—Undoubtedly a contributory influence in general corrosion is the solubility of oxygen in the various solutions.[1] Oxygen is more soluble in an acid than in one of its salts of the same concentration, and more soluble in a salt than in the corresponding base of the same concentration.[2] Furthermore, solubility diminishes with increase in concentration. For this reason (see 1.0 M KCl, 0.1 M KCl and 0.01 M KCl in Table III) corrosion falls off at higher concentrations, and a high enough concentration may completely inhibit it. Such limiting values of concentration have been defined in the corrosion of iron.[3] The divergence of acids and ammonium salts from this behavior may be inferred from what was stated above.

MECHANISM OF COMPLETE CORROSION—As a working hypothesis the following are assumed to be the fundamental reactions in complete corrosion by dissolved oxygen:

$$2Cu + 2H^+ + O \rightleftarrows 2Cu^+ + H_2O \qquad (1)$$

$$Zn + 2H^+ + O \rightleftarrows Zn^{++} + H_2O \qquad (2)$$

The equilibrium may be shifted in the forward direction in three ways:

1—Increase in the concentration of H ions, that is, the acidity.

2—Increase in the concentration of the dissolved oxygen, which varies with different solutions.

3—Removal of the Cu and Zn ions by (a) precipitation as oxide or other insoluble substance, (b) complex ion formation, as $Cu(NH_3)_2^+$ and $Zn(NH_3)_4^{++}$, and (c) oxidation of Cu^+ to Cu^{++}.

This conception of an equilibrium gives a ready explanation of several of the outstanding features of brass corrosion. The well-known fact that alkalies of moderate concentration inhibit corrosion follows from the repression of the H ion. The so-called catalysis by means of dissolved carbon dioxide is explained not so much by the slight increment of H ions as by the removal of Cu and Zn ions by the HCO_3 ion. Those solutions which are the best solvents for oxygen are generally the most corrosive.

OTHER SIGNIFICANT INFLUENCES—The effect of stirring on the speed of corrosion is well known. Contact action is one of the most important factors in corrosion, but the writers have not been able to include it in the present investigation. An illustration came up in one of the manometer experiments. In one of the tests a piece of soft brass stood in a 0.1 M KNO_3 solution for several weeks with no sign of corrosion; but when once a splotch of black CuO appeared at one point, corrosion proceeded rapidly and the stain spread over the whole test piece. This behavior has its analog in the rusting of iron and steel, where the hydrated oxide catalyzes rust formation to a marked degree.[1] Contact with metals nobler than copper strongly catalyzes the corrosion of brass.

The nature of the surface seems of significance. Pieces of brass which have been etched chemically, corrode more rapidly than polished pieces.[2] This may be partly due to increase in surface. Corrosion usually begins at the edge of the test piece, indicating that the strained condition caused by the cutting leaves the edges in a more reactive form. In a few cases corrosion started on the scorings left in rolling the sheet brass at the mill. This behavior is comparable to that of steels,[3] where strains in the metal affect its corrodibility to a noticeable extent.

SUMMARY

The experiments described above point very decidedly to the conclusion that there are two kinds of brass corrosion, *viz.*, electrolytic and complete.

The specific influences of various factors in corrosion may be summarized as follows:

1—High concentration of electrolytes favors electrolytic corrosion in an additive way, and retards, or even inhibits, complete corrosion.

2—Elevated temperatures favor electrolytic corrosion, but diminish complete corrosion by diminution of dissolved oxygen.

3—Contact with metals nobler than brass favors electrolytic corrosion, and is without influence on complete corrosion.

4—Dissolved oxygen has no appreciable effect on electrolytic corrosion, but is essential to complete corrosion.

5—The presence of ions or groups that combine with zinc and copper ions to form compounds of low ionization favors both electrolytic and complete corrosion.

6—There is no specific influence of ions in electrolytic corrosion except in the case of ions that form complexes of low ionization and in the case of hydrogen ion; on the other hand, there is marked specificity in complete corrosion, believed to be largely determined by oxygen solubility.

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[1] *Trans. Far. Soc.*, **5** (1909), 68; *J. Am. Chem. Soc.*, **33** (1911), 362; American Public Health Association, "Standard Methods for Water Analysis Analysis," **1917**, 68.

[2] Giffcken, *Z. physik. Chem.*, **49** (1904), 257.

[3] Friend, *Loc. cit.*, p. 131.

[1] Friend, *Loc. cit.*, p. 96.

[2] Eden, Rose and Cunningham, *Proc. Brit. Inst. Mech. Eng.*, [3 and 4] **1911**, 839; Moore, *Mech Eng.*, **41** (1919), 731.

[3] Hambuechen, Univ. of Wisconsin Bulletin, *Engineering Series* **8** (1900); Heyn and Bauer, *J. Iron Steel Inst.*, **1** (1909), 109.

7—Homogeneity reduces electrolytic corrosion, and has no effect on complete corrosion.

8—Other influences—catalysis, nature of surface, strained areas in the alloy, etc.—are operative, but have not been included in this investigation.

It is doubtful whether in practice either form of corrosion ever occurs to the exclusion of the other. In complete corrosion, dezincification occurs as a secondary process by the displacement of copper from the solution, and since electrolytic corrosion usually takes place in contact with the air, primary oxidation of the alloy is possible.

GASOLINE FROM NATURAL GAS. I—METHOD OF REMOVAL

By R. P. Anderson

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Received December 31, 1919

The hydrocarbon content of natural gas consists essentially of a mixture of such hydrocarbons of the paraffin series as exert an appreciable vapor pressure at the temperature of gas production. Similarly natural gas gasoline consists essentially of a mixture of those hydrocarbons of natural gas that may exist in liquid form at atmospheric temperatures and pressures. As natural gas hydrocarbons, there may be included the normal and various isomeric compounds from methane to undecane, inclusive; and as constituents of natural gas gasoline, all of the natural gas hydrocarbons except methane, ethane, propane, and butane. For convenience of reference, various data concerning the normal paraffin hydrocarbons from methane to undecane, inclusive, are given in Table I.

The constituents of natural gas gasoline may be removed from natural gas and collected in liquid form by either the *compression*, the *refrigeration*, or the *absorption* method. In the general discussion which follows no attempt will be made to consider details of apparatus or operation; on the contrary, the present purpose is merely to present briefly the principles and applications of the different methods and to bring out the relationships that exist between them.[1]

COMPRESSION METHOD

The compression method for the production of gasoline operates on the well-understood principle that the vapor pressure of a substance is independent of the pressure on the gas of which the vapor forms a part. Accordingly, when the pressure on the gas is increased, the partial pressure of the vapor increases only until its saturation pressure is reached, and from this point, increase in pressure results in condensation of increasing amounts of the vapor as liquid. The amount of the substance remaining in vapor form is inversely proportional to the number of compressions employed, using the pressure at which the partial pressure becomes equal to saturation pressure as a basis. For example, if a gas is saturated with pentane vapor at atmospheric pressure, compression to 2 atmospheres will condense one-half the pentane; if the gas is one-tenth saturated, compression to 10 atmospheres will be necessary to increase the partial pressure to the saturation point and this last pressure must be doubled to cause condensation of one-half the pentane vapor.

Such difficulties as are encountered in the efficient operation of a compression plant result from the simultaneous condensation of the several mutually soluble hydrocarbons that constitute natural gas gasoline. What is true when pentane is the only condensable substance no longer holds when other condensable substances are present. The saturation pressure for each gasoline hydrocarbon is influenced by the other condensable hydrocarbons and varies as condensation becomes more and more nearly complete. The result is that the most efficient method of operating a compression plant for the production of gasoline can be determined, at the present time, only by experiment.

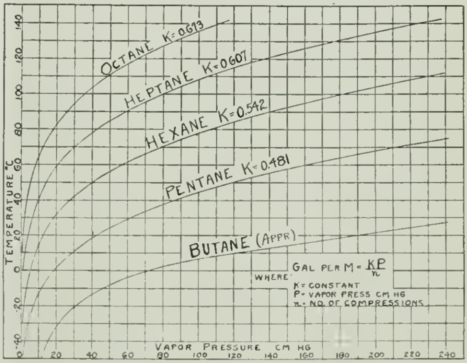

FIG. 1

In actual practice the degree of compression varies from a few pounds to about 300 lbs., depending upon the kind of gas being treated. In some cases a high vacuum is maintained on old wells in oil-bearing sands from which the original gas has almost entirely been withdrawn. The more volatile portions of the oil are gradually vaporized and only a slight pressure is required to condense these as gasoline after they reach the surface of the earth. On the other hand, some natural gases give no condensation of gasoline at 300 lbs. pressure. Gases that yield much less than 0.5 gal. per M cu. ft. of gas at 300 lbs. pressure are not usually compressed for their gasoline content. Additional condensate may usually be obtained by using pressures higher than 300 lbs., but butane and propane are its principal constituents and these of course cannot be retained by themselves in liquid form at atmospheric pressure and room temperature. There is no question but what butane may remain in solution in

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[1] For details, consult the following publications of the Bureau of Mines: "The Condensation of Gasoline from Natural Gas," by Burrell, Seibert and Oberfell, *Bulletin* **88** (1915).

"Extraction of Gasoline from Natural Gas by Absorption Methods," by Burrell, Biddison and Oberfell, *Bulletin* **120** (1917).

"Recovery of Gasoline from Natural Gas by Compression and Refrigeration," by Dykema, *Bulletin* **151** (1918).

"Recent Developments in the Absorption Process for Recovering Gasoline from Natural Gas," by Dykema, *Bulletin* **176** (1919).

TABLE I—PROPERTIES OF NATURAL GAS HYDROCARBONS

	A	B	C	D	E	F	G	H	I	J	K	L
		Melting Point		Boiling Point		Specific Gravity						
NAME	Formula	° C.	° F.	° C.	° F.	Gas Air = 1	Liquid Water = 1	Gravity Baumé Scale	Vapor Pressure 60° F. In. Hg	Cu. Ft. Vapor per Gal.	Gal. per M Cu. ft. Sat. Vapor	B. t. u. per Cu. ft.
Methane	CH_4	—184.0	—299.0	—160.0	—256.0	0.554	...	...	...	. .	. .	1008.5
Ethane	C_2H_6	—172.1	—277.8	—84.1	—119.4	1.038	...	...	...	. .	. .	1763.2
Propane	C_3H_8	—187.8	—206.2	—44.1	—47.4	1.523	...	...	...	. .	. .	2518
Butane	C_4H_{10}	—135.0	—211.0	+0.3	+32.5	2.007	0.600	103.3	63.00	. .	. .	3273
Pentane	C_5H_{12}	—130.8	—203.4	36.4	97.7	2.491	0.626	93.6	13.99	27.3	17.1	4027
Hexane	C_6H_{14}	—94.0	—137.2	69.0	156.2	2.975	0.663	81.2	3.82	24.2	5.26	4782
Heptane	C_7H_{16}	—97.1	—142.8	98.4	209.2	3.459	0.688	73.5	1.02	21.6	1.57	5537
Octane	C_8H_{18}	—56.6	—69.9	125.5	257.9	3.944	0.707	68.0	0.31	19.5	0.53	6291
Nonane	C_9H_{20}	—51.0	—59.8	150.5	302.9	4.428	0.722	63.9	0.16	17.7	0.30	7046
Decane	$C_{10}H_{22}$	—32.0	—25.6	173.0	343.4	4.912	0.734	60.7	0.08	16.2	0.16	7801
Undecane	$C_{11}H_{24}$	—25.6	—14.1	194.5	382.1	5.396	0.743	58.4	0.03	15.0	0.07	8555

COLUMNS B AND D—The values for the melting and boiling points that are given in Columns B and D were taken from the 1918 edition of Van Nostrand's "Chemical Annual." The boiling point of ethane was determined at a pressure 749 mm., and that of nonane at 759 mm.; otherwise the figures are for 760 mm.

COLUMN F—Theoretical specific gravities are given in Column F. They were computed from the formula sp. gr. = $0.4842\,n + 0.07$, in which n represents the number of carbon atoms in the hydrocarbon molecule (see Anderson, THIS JOURNAL, **11** (1919), 299).

COLUMN G—The figures in Bernthsen's "Organic Chemistry," 1912 Edition, page 30, form the basis of Column G, corrections having been applied to obtain the ratio of the weights of hydrocarbon and water at 60° F. No correction has been made to the value for butane which was determined at its boiling point.

COLUMN H—The Baumé scale figures in Column H were computed from the values in Column G by the formula: Degrees, Baumé = $\frac{140}{\text{Sp. Gr. } 60°/60° \text{ F.} - 130}$, in accordance with the procedure adopted by the Bureau of Standards. (See *Circular* **57**.)

COLUMN I—The vapor pressures at 60° F. given in Column I were taken from curves prepared from tables in Landolt-Börnstein, "Physikalisch-chemische Tabellen," with the exception of the values of nonane and undecane, which were gotten from the others by interpolation.

COLUMN J—The volume of dry vapor at 60° F. and 30 in. mercury corresponding to one gallon of the important gasoline hydrocarbons, as given in Column J, was computed from the formula:

$$\frac{\text{Wt. gallon water at } 60° \text{ F.} \times \text{Sp. Gr. Hydrocarbon (Water} = 1)}{\text{Wt. cu. ft. dry air at } 60° \text{ F. 30 in. Mer.} \times \text{Sp. Gr. Hydrocarbon (Air} = 1)} = \frac{8\ 328}{0.07650} \times \frac{\text{Sp Gr. Hydrocarbon (Water} = 1)}{\text{Sp. Gr. Hydrocarbon (Air} = 1)}.$$

COLUMN K—Column K shows the theoretical yield of the various gasoline hydrocarbons expressed in gal. per M cu. ft. of gas at 60° F. and 30 in. mercury. The yields were computed by the formula: Gal. per M cu. ft. = $\frac{\text{Vapor Pressure}}{30} \times \frac{1000}{\text{Cu. ft. per gal.}} = \frac{\text{Vapor Pressure} \times 33.3}{\text{Cu. ft. per gal.}}$.

COLUMN L—The heating value of dry gas at 60° F., 30 in. mercury, as given in Column L, was computed from the formula: B. t. u. per cu. ft. = $253.8 + 754.7\,n$, in which n represents the number of carbon atoms in the hydrocarbon molecule.

natural gas gasoline for considerable periods of time at temperatures of 60° to 70° F., but the losses of true gasoline constituents along with the butane make it undesirable to condense much of the latter in the process of gasoline manufacture.

The heat of compression of the gas is usually removed by cooling with water. It is possible to cool the gas to about 50° F. by the use of deep-well water, or to even lower temperatures by the use of creek water in the winter time in certain localities, but it is probable that, on the average, the gas from which gasoline is to be obtained is not cooled below 60° F. by the use of water. The temperature to which the compressed gas is cooled is an important thing from the point of view of efficiency of condensation, as will be readily understood from an inspection of Fig. 1, which contains pressure-temperature curves of the normal paraffin hydrocarbons, butane to octane, inclusive. To illustrate the importance of this cooling, the maximum pentane content of a gas is 35 per cent less at 50° than at 70° F., the hexane content 38 per cent less, and the heptane content 48 per cent less. To accomplish the same result by increasing the pressure, while maintaining the temperature at 70° F., the number of compressions would have to be increased by 54 per cent in the case of pentane, by 61 per cent in the case of hexane, and by 92 per cent in the case of heptane.

REFRIGERATION METHOD

Refrigeration methods are sometimes resorted to in order to lower the temperature of the gas below that which may be obtained by the use of air or water. The usual procedure is to utilize the cooling effect obtained by the expansion of the compressed gas, especially in those cases where it is not necessary to deliver the gas at high pressure. The expansion may take place through an orifice or valve, or in an expansion engine, the cooled expanded gas being made to absorb heat from the high pressure gas in various forms of heat exchanger of the counter-current type. The cooling effect that is obtained through an orifice or valve is small and generally quite unsatisfactory. By the use of expansion engines, the temperature of the high pressure gas may be cooled to 0° F., or lower if desirable. The expansion engine has not as yet been widely used in the eastern states.

ABSORPTION METHOD

If a mineral oil is placed in contact with natural gas, it dissolves a portion of each of the hydrocarbons present in the gas, the percentage efficiency of the absorption increasing with the molecular weight of the hydrocarbon. If this oil be subsequently heated, a gas is liberated which differs from that which was treated with the oil in that it contains a much higher concentration of the heavier, or gasoline, hydrocarbons. If this liberated gas be cooled, condensation of gasoline may occur, and additional gasoline may be obtained by compressing and re-cooling this gas. In a word, then, the absorption process of producing natural gas gasoline consists in the preparation from a natural gas of an artificial gas mixture in which the greater part of the gasoline-forming hydrocarbons of the natural gas have been concentrated and from which gasoline may easily be condensed by application of the principles of the compression method.

It is evident then, from this point of view, that the absorption method is especially suited to the treatment of natural gases from which gasoline cannot be condensed, or at best only very incompletely, by direct compression and cooling.

In practice, natural gas is treated continuously with the absorbing oil, quite commonly at pressures considerably above atmospheric, in vertical absorbers in which the gas enters at the bottom and leaves at the top, and oil enters at the top and leaves at the bottom. After leaving the absorber the course of the oil is normally as follows: From the absorber through a trap to the vent tank where the gas liberated from the oil as a result of the drop in pressure is withdrawn; from the vent tank to the still through a heat exchanging and vapor rectifying system; and from the still to the absorber through the heat exchanger in the direction opposite to that followed on its way to the still, through the oil cooler, and finally through the oil pump. The gas that is liberated in the still passes through the rectifier to remove any oil that it may carry, through a condenser for the condensation of whatever gasoline may be obtained at pressures only slightly above atmospheric, and then through a compressor and second condenser for the separation of such gasoline as can be secured.

The proper design and method of operation of an absorption plant must be determined for each different plant. At the present time it would be rare indeed to build a plant to fit a particular need that would not require modifications after it is put into use, and the most efficient method of operation can be determined only after an extended period of experimentation.

It may be estimated that the average absorption plant operates at an efficiency of 50 to 60 per cent, computed on the actual gasoline content of the gas, although some few plants may perhaps reach efficiencies of 70 to 80 per cent. The highest efficiency that it is practicable to maintain will vary considerably with the individual conditions, but it is safe to state that this efficiency has not yet been reached, and will not be reached until thorough investigations have been made in the matters of plant design and plant operation.

CHOICE OF METHOD

For the purpose of considering what method, or methods, should be employed in recovering gasoline from natural gas, the following classification may be made: (1) Lean gas, containing less than 0.5 gal. gasoline per M cu. ft. of gas; (2) moderately rich gas, containing from 0.5 to 3 gal. gasoline per M cu. ft. of gas; (3) rich gas, containing more than 3 gal. gasoline per M cu. ft. of gas.

1—Lean gas is usually compressed for the purpose of transporting it to the point of consumption, but this compression would not ordinarily cause the condensation of gasoline. The absorption method may be employed on gas of this character, provided its gasoline content is sufficient to make the project a financial success. The absorption method has been successfully employed where the gasoline production has amounted to less than 0.1 gal. per M cu. ft. of gas.

2—The compression of a moderately rich gas for transmission purposes may not result in the condensation of gasoline if the pressure required is low, but gasoline will be condensed if high pressures are necessary. In a gas of this sort the gasoline removal will by no means be complete, even at high pressures, on account of the low initial partial pressures of the gasoline hydrocarbons, and either the refrigeration or the absorption method may be applied on the residual gas, the choice depending upon the local conditions. If the absorption method is to be employed, the pressure need not be raised above the point required for transmission of the gas, while if the refrigeration method is to be employed, the gas should be compressed to 250 to 300 lbs. before expansion, according to the usual procedure.

3—A rich gas should be compressed primarily for its gasoline content. In this case, on account of the higher initial partial pressure of the gasoline constituents, the efficiency of gasoline extraction will be much higher than in the previous case and treatment of residual gas by refrigeration or absorption method would yield but little gasoline of marketable character. To treat a rich gas by the absorption method at low pressure is an alternative that may possibly have desirable features in exceptional cases.

It will, of course, be understood that no definite figures can be given for the gasoline content at which the direct compression method begins to be applicable, nor for the gasoline content at which the compression method can be made so efficient that no treatment of residue gas is advisable. The figures that have been given for the purpose of setting limits between Classes 1, 2, and 3 are, therefore, only approximate and dependent to a considerable extent upon the nature of the gas to be treated.

SUMMARY

I—The principles forming the foundation of the *compression*, *refrigeration* and *absorption* methods for the production of gasoline from natural gas have been enunciated and the relationships between the different methods have been explained. Incidentally, it has been shown that the absorption method is essentially an indirect compression method, in which the gasoline-forming constituents of a gas are concentrated in small space by fractional solubility before the compression method is applied.

II—A table of properties of the principal gasoline constituents and curves showing the vapor pressures of some of these hydrocarbons at different temperatures have been inserted for convenience of reference.

III—The applications of the different methods have been discussed. The absorption method is employed exclusively for lean gas and the compression method almost exclusively for rich gas. For moderately rich gas, the production may be largely by the compression method, or largely by the absorption method, as the situation demands.

THE USE OF PARACOUMARONE RESIN IN VARNISHES

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Received January 9, 1920

Paracoumarone resin, the artificial resin prepared by the polymerization of the coumarone and indene in certain aromatic naphthas, is now manufactured and sold in considerable quantities in the United States, and is finding application in various industries. The process for the manufacture of this material has recently been so perfected that large quantities of lighter color and higher melting point than that previously obtainable are now available for commercial purposes. This resin possesses certain properties which render it particularly suitable for use as a varnish gum to replace ester gum or the more expensive kauri and other foreign gums. In this laboratory a considerable amount of work has been done to determine the advantages of paracoumarone resin as a varnish gum, the most satisfactory procedure for making varnishes from paracoumarone resin, and the general properties of these varnishes.

GENERAL PROPERTIES OF PARACOUMARONE RESIN

Aromatic naphthas distilling between 160° and 200° C. contain considerable amounts of indene, coumarone, and their homologs. When such naphthas are agitated with strong sulfuric acid these compounds are polymerized, the polymerization products remaining in solution in the naphtha. Similar polymerization may be effected by the action of certain metallic salts—for example, aluminum chloride—or by simply heating the naphtha under pressure. When the naphtha is separated from the polymerizing agent, neutralized, and distilled to remove unpolymerized material, there remains a liquid residue which, on cooling, solidifies to the resinous material known as "paracoumarone resin."

The technical resin consists essentially of a mixture of the polymerization products of coumarone, indene, and their homologs. The degree of polymerization has not been definitely determined. Some authorities have stated that the resin is a tetra-polymer, while other results have indicated that, in some cases, at least, the resin molecule is built up from eight simple molecules. Some work done in this laboratory has indicated that the resin is at least an octo-polymer, and that the lower values obtained by previous observers were due to the presence of impurities in the resins examined by them.

Chemically, paracoumarone resin differs from the ordinary varnish resins in that it is a neutral body, insoluble in alkalies. It is true that some samples of technical paracoumarone resin have shown an apparent, and very low, "acid number," but this has been due to impurities. The resin is unattacked by acid (with the exception of strong sulfuric acid and nitric acid), ammonia, and soap solution; and is practically insoluble in alcohol. The unusual chemical inertness of paracoumarone is of particular value in connection with its use as a varnish resin, since it renders the varnish films more resistant to alkalies, soap solutions, alcohol, fruit acids, and other materials by which the common varnish resins are attacked.

Physically, paracoumarone resin when properly prepared is a brittle, amorphous material, somewhat resembling rosin in appearance. The poorer grades are black but the varnish grades vary in color from reddish brown (similar to Grade E rosin) through orange-yellow to very pale yellow (similar to WW rosin). Inferior grades may be cloudy, but the varnish grades are clear.

Paracoumarone is apparently not a true solid, but a highly supercooled liquid. When heated, it does not melt sharply, but gradually softens and finally liquefies. It does not, therefore, possess a true melting point. However, an apparent "melting point" may be determined by forming a cube of the material around a copper wire, heating this cube in an air bath under definite and constant conditions, and noting the temperature at which the material becomes sufficiently fluid to drop from the wire. By this test rosin shows a melting point of approximately 100° C., while Manila gum melts at 127° to 135° C. The apparent melting point of paracoumarone resin varies from 85° to 205° C. We have found, however, that paracoumarone with a melting point lower than 125° C. is not suitable for varnish work since varnishes made with the low melting paracoumarone tend to remain tacky for a rather long time. Paracoumarone melting above 145° C. has not yet been prepared in commercial quantities. The varnish grade of paracoumarone now available has a melting point between 125° and 145° C., although it is expected that resin melting above 145° C. can soon be supplied if there is any demand for such high-melting material.

Paracoumarone resin, like rosin and other varnish gums, possesses the property of delaying the polymerization of tung oil by heat, so that a mixture of tung oil and paracoumarone resin may be safely bodied by heating to 300° C., although straight tung oil would polymerize at this temperature.

PREPARATION OF VARNISHES FROM PARACOUMARONE RESIN

We have prepared paracoumarone varnishes of varying oil content, ranging from 5 gal. of oil per 100 lbs. of resin to 40 gal. of oil per 100 lbs. of resin. In all of these varnishes the oil used has been a mixture of 15 parts of pure raw linseed oil and 100 parts of China wood oil. Cobalt linoleate was used as the drier, using 1.5 lbs. of drier per 100 lbs. of oil. In most of these varnishes we have used, as a thinner, a heavy, refined, coal-tar paint solvent distilling completely above 160° C., although some lots have also been made up with pure gum turpentine, petroleum base turpentine substitute, and other turpentine substitutes. We have confined our work so largely to varnishes thinned with the coal-tar solvent because we have found that such varnishes are in every respect equal to varnishes thinned with the more expensive turpentine. The varnishes thinned with petroleum naphthas have not always been satisfactory because some of these naphthas have contained enough paraffin to cause a slight dulling of the films from the varnishes made from them, and because some of these varnishes have shown a tendency to become turbid when allowed to stand at temperatures below 32° F.

The most satisfactory procedure for making up these paracoumarone varnishes was found to be as follows:

Place the mixed linseed and China wood oil in the varnish kettle and add the required amount of paracoumarone resin, preferably broken up into fairly small lumps. Heat the mixture at the rate of about 2.5° C. (4.5° F.) per minute to a final temperature of 290° to 320° C. (555° to 610° F.). (The temperatures given are corrected for the emergent stem of the thermometer.) We have found that with the resins having the higher melting points it is essential to carry the heating to the higher temperatures in order to obtain thorough incorporation of the resin with the oil, and to prevent the clouding and wrinkling of films made from the finished varnishes.

When the desired final temperature is reached, remove the kettle from the fire and allow the mixture to cool. As soon as the temperature has fallen to near the boiling point of the thinner to be used, add the thinner and mix well. The amount of thinner is, of course, determined by the type of varnish and by the desired final viscosity of the varnish. When the thinned mixture has cooled to well below 100° C., add the required amount of drier solution, prepared by adding 100 parts of cobalt linoleate (cut in thin pieces) to 84.2 parts of raw linseed oil, heating the mixture to 200° C. for 2 hrs., adding 42.1 parts of bodied China wood oil, continuing the heating (with frequent stirring) at 200° C. for one hour, cooling to 160° C., and pouring the resulting solution into 600 parts of coal-tar naphtha paint solvent. The final drier solution contained 1.03 per cent of cobalt.

PROPERTIES OF PARACOUMARONE RESINS

All of the varnishes which have been prepared have been clear and free from sediment. In color they have been as light or lighter than the commercial varnishes now on the market. The color of the finished varnish, of course, depends upon the color and amount of the original paracoumarone resin. The very pale varnish-grade resins give very light varnishes, which, when properly applied, dry to form almost colorless films; while the darker grades give slightly yellowish films.

All of the varnishes, when properly applied, set to the touch in 3 hrs. and dried hard in less than 20 hrs. The resulting films were clear and free from cloudiness and tackiness, smooth, brilliant, and very light in color.

The rubbing qualities of the varnishes were determined by the following test:

To a maple panel (18 in. by 6 in.) was applied a coat of varnish, well rubbed in, which was allowed to dry for 48 hrs. and was then lightly sandpapered. A second coat was then applied, allowed to dry for 48 hrs., and lightly sandpapered. A third coat was applied, allowed to dry for 72 hrs., polished to a satin finish with ground pumice and water, and finally polished with a little linseed oil.

All of the varnishes, from the 5 gal. varnish to the 40 gal. varnish, inclusive, gave smooth coats, free from imperfections and with a smooth, satiny luster.

The water-resisting properties of the varnishes were determined by the following test:[1]

Basswood panels were filled with a coat of drop black oil, thinned with turpentine and drier, and allowed to dry for at least 10 days. Two successive coats of varnish were then applied, the first coat being allowed to dry for 48 hrs., and lightly sandpapered. When the second coat had dried for 72 hrs. the panel was placed at an angle of 45° and a gentle stream of cold water was allowed to flow down the middle of it for 18 hrs. A small stream of boiling hot, distilled water was allowed to flow on another portion of the panel for 20 min. All of the varnishes formed films which withstood perfectly the action of the cold water, showing no dulling, whitening, or other effects. The 10, 15, and 20 gal. varnishes stood up perfectly under the hot water test. The 5 gal. varnish, after exposure to the hot water test, showed a very faint, cloudy surface film which was apparent only on close inspection, and which was readily and completely removed by polishing with a little linseed oil.

Weathering tests on panels coated with the 5, 10, 15, 20, 30, and 40 gal. varnishes, respectively, showed that they were fully as resistant to weathering as any of the varnishes of similar oil content now on the market. The long-oil varnishes from paracoumarone resin stood up particularly well under this test, being noticeably more resistant to weathering than was any one of the eight standard commercial spar varnishes used for comparison purposes. In hardness, toughness, and elasticity, the varnish films from paracoumarone varnish were similar to the films from the best commercial varnishes.

We have found that the cobalt linoleate may be replaced by a manganese drier (acetate or linoleate) with equally satisfactory results, although a somewhat larger amount of the manganese drier is required to give the same drying time. The use of manganese dioxide as a drier has not been altogether satisfactory, as it causes the varnish to darken.

From these results, it is apparent that varnishes properly prepared from paracoumarone resin (m. p. 125° to 145° C.), China wood oil, linseed oil, cobalt or manganese (acetate or linoleate) drier, and heavy refined coal-tar naphtha are light in color, have excellent drying and rubbing qualities, and are as tough, as hard, and as resistant to hot and cold water and to weathering as are the best commercial varnishes.

ADVANTAGES OF PARACOUMARONE RESIN AS A VARNISH GUM

In considering the advantages to be gained by using paracoumarone resin as a varnish gum, the following facts must be taken into consideration:

1—Paracoumarone resin can be obtained at a price approximately equal to that of ester gum, and much below that of the better grades of kauri and other imported gums.

2—It is offered for sale in quantity in a number of different grades, so that material of the desired melting point and color can be secured.

3—It is free from dirt, sticks, etc., so that the varnish manufacturer is relieved of the trouble and expense of sorting or purifying the resin or of settling or filtering the varnish to remove impurities due to dirt in the resin.

4—It contains essentially no material which is volatilized during the "cooking" of the varnish. Thus all of the resin remains in the finished varnish, while rosin and other varnish gums are partially decomposed during the "cooking" giving volatile products and allowing only a portion of the resin to remain in the varnish.

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[1] Based on test described in U. S. Railroad Administration Specifications for Spar Varnish, May 1, 1918.

5—The remarkable chemical inertness of paracoumarone renders the varnishes very resistant to the action of ammonia, lye, soap, and other alkalies; vinegar, fruit acids, and other acids; and alcohol or alcoholic solutions.

THE WEARING QUALITY OF EXTERIOR VARNISHES COMPARED WITH THEIR PHYSICAL AND CHEMICAL ANALYSES

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Received December 4, 1919

INTRODUCTION

The varnishes used were purchased in quart or half-gallon cans from stores, or sent in by the manufacturer for the purpose of this investigation, and, in most cases, represent the better grades of the product. All were exterior varnishes except Nos. 11, 12, and 13, which were interior varnishes included for purposes of comparison. A similar study of a large number of interior and floor varnishes is in progress.

The status and reliability of methods of varnish analysis have already been discussed by the writer.[1] It is the aim of this and subsequent investigations to obtain such data that both the public and the varnish maker may determine the true value of any varnish. Some of the most vital questions are: How little oil may a varnish contain and still be good? What must be the limits of the resin-oil ratios in exterior, interior, floor, and automobile varnishes? What must be the limit to the amount of thinner used? How much rosin may a varnish contain?

SERVICE TEST

The doors of several buildings on the college campus were selected, so that each varnish would have a northern, eastern, southern, and western exposure, and so that in three cases all of them would be on the same piece of wood. In other cases, two were placed on the same piece of wood and the positions so varied that they would be acted upon in the same way. On the north doors and wooden pillars of one of the buildings all the varnishes were in three cases placed on the same piece of wood, the old film was entirely removed, and one coat of liquid filler and two coats of varnish applied, the filler and first coat being rubbed down with fine emery paper. The wood was measured and a definite amount was allotted to each varnish. In all other cases the old coat was rubbed smooth and three coats of varnish were applied.

At the end of 9 mos. exposure the luster and condition (checking, cracking, washing, whitening) of the film were studied. Three months later another thorough study was made. The results were in excellent agreement with each other and showed that fair methods were used. It will be necessary to make a third examination at the end of 2 yrs. service to differentiate between the better varnishes.

OTHER PHYSICAL TESTS

The color, clearness, odor, consistency, and working and flowing under the brush were first noted; then the viscosity, specific gravity, elasticity, and time of drying. These tests were followed by noting brilliancy, uniformity of film, and the effect of water upon panels of wood coated with the varnish.

CHEMICAL ANALYSIS

The percentages of total resins, rosin, total oils, turpentine, turpentine substitutes, and ash were determined with reasonable accuracy. We have not attempted as yet to identify the resin although this will be taken up within the next few months.

METHODS OF MAKING PHYSICAL TESTS

VISCOSITY—An Engler viscosimeter was used for the viscosity and the usual method was followed, 100 cc. of the varnish being allowed to run out.

SPECIFIC GRAVITY—A Westphal balance was sufficiently accurate for the specific gravity determination.

TIME OF DRYING—A thin coat of varnish was applied to a glass plate and allowed to stand away from the dust at an angle of 60°. The coat was examined frequently and the time required for drying recorded.

ELASTICITY—The glass plate used in the drying test was scratched with a knife, and the smoothness of the cut was noted. A heavy sheet of cardboard was then coated with simple sirup and a coat of varnish applied. When this had dried, the film was removed by placing the cardboard in water. At definite intervals the elasticity was determined as follows: A half-inch strip of film was clamped at both ends between two smooth pieces of wood. One end was clamped to an arm attached to a vertical wooden beam nailed to a heavy base. On the beam was placed a metric scale and one of the binders on the free end of the film served as an indicator. A weight was hung from a wire stirrup attached to the free end, and the distance in millimeters which the film stretched before breaking constituted the measure of the elasticity.

BRILLIANCY, LUSTER AND SPONGE TEST—The varnished panel was examined for luster and uniformity of coat, considering nearly all of the varnishes at the same time and comparing them with each other. A sponge made of felt was placed on one end of the panel and kept moist for a definite period of time. If the varnish failed to whiten, the panel was placed in water for definite periods. It was then removed and allowed to dry before examination.

METHODS USED IN CHEMICAL ANALYSIS

VOLATILE THINNER—Fifty grams of varnish were weighed into a half-liter Erlenmeyer flask, and subjected to steam distillation, the flask being heated in an oil bath at 130° C. until no more volatile oil was carried over. The distillate, usually 500 cc. in volume, was collected in a separatory funnel and allowed to settle, the water run off, and the oil transferred to a tared flask and weighed. In calculating the volatile thinner it was assumed that the water which distilled over had dissolved 0.4 g. per 100 cc. (We did not use the values obtained by this method, as the non-volatile method is more accurate.)

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[1] This Journal, 11 (1919), 200.

TABLE I—PHYSICAL AND CHEMICAL TESTS

	Physical Tests							Chemical Tests[2]						
No.	Color[1]	Smell	Sp. Gr. 29.5° C.	Consistency	Viscosity Engler 30° C.	Working and Flowing	Drying Hrs.	Volatile Thinner	Benzine in Vol. Thinner	Total Resins	Rosin	Total Oils	Ash	China Wood Oil (Approx.)
1	10th	Good	0.9269	Fair	22.44	Slightly sticky	29.25	41.00	35.49	26.86	5.30	33.09	0.41	60
2	4th	Good	0.9229	Heavy	34.86	Slightly sticky	29.25	40.64	44.27	29.80	2.50	29.40	0.16	60–80
3	3rd	Good	0.9247	Heavy	54.12	Good	30.5	47.70	40.34	25.46	4.05	26.28	0.19	60
4	6th	Strong	0.9324	Light	12.67	Good	26	39.30	23.21	26.24	2.86	34.09	0.36	20
5	5th	Strong	0.9229	Light	17.13	Good	26	50.82	16.79	19.90	4.30	28.94	0.34	80
6	8th	Good	0.8959	Fair	16.85	Good	26.5	46.84	52.80	24.52	7.30	28.03	0.61	40–50
7	1st	Peculiar	0.9160	Medium	14.95	Good	23.5	56.41	0.0	17.47	5.04	26.55	0.57	33.33
8	7th	Good	0.9317	Fair	27.22	Good	23.5	49.40	51.26	22.31	6.36	27.05	1.24	10–20
10	2nd	Peculiar	0.9169	Light	22.32	Slightly sticky	26.5	53.94	0.0	19.05	5.64	26.04	0.97	70–80
11	?	Good	0.9315 at 25°	Medium	42.65 at 25°	Good	12	37.48	56.34	45.78	17.28	16.74	0.17	33.33
12	?	Good	0.9072 at 25°	Medium	17.47 at 25°	Good	12	43.47	49.25	27.80	6.09	28.53	0.20	33.33
13	...	.....	....	.....	....	.....	...	45.86	58.25	33.73	6.74	19.73	0.68	50

[1] Marked in order of paleness. Colors 1st and 2nd are very pale.

[2] All values are given in percentages of the constituent in the varnish, except "Benzine in Vol. Thinner" and "China Wood Oil" which are percentages in the "Volatile Thinner" and "Total Oils," respectively. No fish oils were detected.

TABLE II—PANEL AND FILM TEST

				Elasticity		
No.	SPONGE[1]	BRILLIANCY	SURFACE	Scratch	Break[2]	Exposure 60 Days
1	Dull and whitened	Good	Fair	Fair, some scale	9, 11.4, 10	Poor luster
2	Dull and somewhat whitened	Good	Fair	Fair, some scale	11.3, 11.9, 11.4, 9.2	Good
3	Dull and whitened	Poor	Fair	Very good, very little scale	14.2, 11.4, 13.5, 10.1	Some washing
4	Somewhat dull and whitened	Fair	Good	Very good, very slight scale	13.6, 11.1, 10.5	Good
5	Trace of dullness and whiteness	Good	Good	Very good, very slight scale	13.1, 11.5, 12.4	Good
6	No effect	Good	Good	Excellent, no scale	13.3, 12.9, 12.8, 12.5	Good
7	Trace of dullness and whiteness	Good	Good	Excellent, no scale	11.6, 12.0, 13.1, 11.8	Good
8	Trace of dullness and whiteness	Fair	Good	Excellent, no scale	10.5, 10.4, 13.6, 10.9	Good
10	No effect	Good	Fair	Excellent, no scale	11.9, 13.1, 13.0, 13.4	Good
11	Dull and whitened badly in 3 hrs.	Very poor	Very poor	....	....	.....
12	Slightly dull but no whitening	Fair	Fair	....	....	.....

[1] No whitening occurred until left in water 8 hrs. in all cases except 11.

[2] The figures, minus 7.0, represent the number of centimeters the 0.5 in stretched under the pull of a weight which was the same for the same or nearly the same age. Where there are four readings the age was 6, 16, 35, and 76 days, respectively, and for the others it is 5, 15, and 35 days.

BENZINE AND OTHER PETROLEUM PRODUCTS IN THE VOLATILE THINNER—Five cc. of the volatile matter were placed in a 50 cc. graduated tube which was clamped to an iron stand and suspended in cold water. A mixture containing 4 parts of concentrated and one part of fuming sulfuric acid was added in 5-cc. portions, and the tube shaken after each addition and allowed to cool before adding the next portion. If all action had ceased after 25 cc. had been added, the tube was allowed to stand one hour and the volume of thinner that remained read off. It was well to take a reading after another hour to insure complete settling. The volatile thinner remaining consisted of benzine or other petroleum fractions and the percentage by weight was calculated in the following way:

$$\text{Per cent benzine (by vol.)} \times 74 + [(100 - \text{per cent benzine}) \times 0.86] = \text{av. sp. gr.}$$

$$\text{Wt. of sample} = \text{av. sp. gr.} \times 5$$

$$\text{Wt. of benzine} = \text{vol. benzine} \times 74$$

$$\text{Per cent benzine (by wt.)} = \frac{\text{wt. benzine}}{\text{wt. sample}}\ 100$$

NON-VOLATILE MATTER AND ASH—Between 25 and 50 g. of the varnish were weighed into a 3-in. porcelain evaporating dish and heated in a drying oven at 110° to 120° C. until the weight became constant. The loss in weight divided by weight of sample multiplied by 100 gave the percentage of volatile thinner, *i. e.*, turpentine and turpentine substitutes. It was then ignited, care being taken to prevent boiling over, cooled, and weighed The residue constituted the ash. 100 — (per cent of volatile thinner + per cent of ash) = per cent total resin and oil.

RESIN AND OIL (*Boughton's Method Somewhat Modified*)—From 4 to 6 g. of varnish were weighed into a 125-cc. Erlenmeyer flask, 25 cc. of water added, and the mixture boiled over a very small flame until only a few cc. of water remained. 25 cc. each of 0.5 *N* alcoholic potash and benzene were added, and the mixture refluxed for one hour. The solution was then evaporated to about 10 cc. and transferred to a 500-cc. separatory funnel, washing the flask with alcohol, water, and ether. (In this and all other similar operations ice-cold ether and ice-cold water were used and small quantities of alcohol added when needed to break the emulsion. 100 cc. each of water and ether were added and the mixture well shaken. The shaking was repeated 3 times. The ether layer was well washed with water, and separated. (A weighed Erlenmeyer flask labeled "Gums" was used to receive this ether layer from the separatory funnel.) The flask, containing the first part of resins separated from the other constituents, was set aside, and used only to receive ether extracts of resins or unsaponifiable matter.

The aqueous layer and washings were acidified with hydrochloric acid, completely extracted with ether, and the ether separated from the fatty and resin acids and the remainder of unsaponifiable matter by distillation. To the flask were added 20 cc. of absolute alcohol and 20 cc. of a mixture of 4 parts absolute alcohol with 1 part of concentrated sulfuric acid, and the contents were refluxed for 5 min. The mixture was transferred to a separatory funnel, using ether and water to rinse the flask, 100 cc. of ether added, and the flask shaken; 100 cc. of a 10 per cent solution of sodium chloride were added and the flask again well shaken. The ether layer was separated and washed with water, and the aqueous layer and the washings of the ether layer extracted with 50 cc. of ether. This ether layer was added to the former one, the aqueous layer being discarded. The combined ether extracts were treated in the funnel with 50 cc. of 0.2 *N* aqueous potassium hydroxide and 10 cc. of alcohol and well shaken after the layers had separated at least twice. The layers were separated, the ether layer shaken with 50 cc. of water containing 5 cc. of the potassium hydroxide solution and 5 cc. of alcohol, and after settling, the aqueous layer was combined with the original one. These layers were extracted completely with ether and all the ether layers combined and washed. The aqueous

TABLE III—SERVICE TEST

No.	NORTHERN EXPOSURE	SOUTHERN EXPOSURE	EASTERN EXPOSURE	WESTERN EXPOSURE	NORTH LIBRARY DOOR
2	All 3 good	....	1 good out of 1	1 checking out of 9	....
3	All 4 good	....	1 fair out of 1	3 checking out of 9	....
4	1 checking out of 2	All checking entire door	....	....	....
5	3 good, 1 fair out of 4	....	1 washed, 2 checking out of 9	1 good out of 1	....
6	All 5 good	1 good out of 1	....	....	6 checking out of 11
7	All 5 good	....	....	....	4 checking out of 11
8	All 5 good	2 checking out of 9	....	....	1 checking out of 1
13[1]	1 scaling, 2 whitened 1 washed out of 5	....	2 scaling, 1 washing 4 nearly washed off out of 9	....	....

[1] By mistake No. 13, an interior varnish, was used in the test for the exterior No 1. All of the northern exposures were made on the doors to the back entrance of the engineering building, the old varnish being removed, and the wood filled before the test varnishes were applied.

layers were acidified with hydrochloric acid, the resin acids extracted with ether, transferred to the flask labeled "Gums," and the solvent distilled off. The ether layers were transferred to the flask and the solvent removed as before. The residue was refluxed with 25 cc. of 0.5 N alcoholic potash for one hour, and the last of the unsaponifiable matter removed by two or more extractions with 50-cc. portions of ether. The extracts were added to the "Gums" flask, the solvent removed, the contents dried on a steam bath over night, and heated to constant weight in a drying oven at 110° to 120° C. The aqueous layer was acidified as before, completely extracted with ether, and the ether layers washed with water. The ether layer was transferred to the flask and the solvent removed. The flask and contents were heated on a steam bath over night or until all the water was removed, and then heated in the oven along with the "Gums" to constant weight.

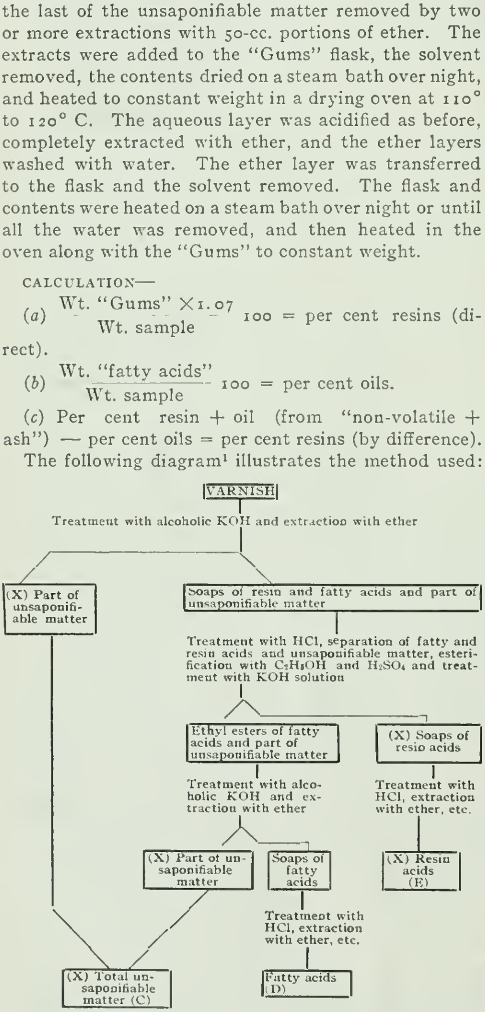
CALCULATION—

(*a*) $\frac{\text{Wt. “Gums”} \times 1.07}{\text{Wt. sample}}$ 100 = per cent resins (direct).

(*b*) $\frac{\text{Wt. “fatty acids”}}{\text{Wt. sample}}$ 100 = per cent oils.

(*c*) Per cent resin + oil (from "non-volatile + ash") — per cent oils = per cent resins (by difference).

The following diagram[1] illustrates the method used:


VARNISH
Treatment with alcoholic KOH and extraction with ether
(X) Part of unsaponifiable matter
Soaps of resin and fatty acids and part of unsaponifiable matter
Treatment with HCl, separation of fatty and resin acids and unsaponifiable matter, esterification with C₂H₅OH and H₂SO₄ and treatment with KOH solution
Ethyl esters of fatty acids and part of unsaponifiable matter
(X) Soaps of resin acids
Treatment with alcoholic KOH and extraction with ether
Treatment with HCl, extraction with ether, etc.
(X) Part of unsaponifiable matter
Soaps of fatty acids
(X) Resin acids (E)
Treatment with HCl, extraction with ether, etc.
(X) Total unsaponifiable matter (C)
Fatty acids (D)

DETERMINATION OF ROSIN. *Qualitative*—Rosin was detected qualitatively as follows: 5 cc. of the varnish were poured into a small separatory funnel and 5 cc. of carbon bisulfide were added, the mixture shaken, and 10 cc. of acetic anhydride added. After complete separation into layers, 1 or 2 cc. of the lower acetic anhydride layer were poured into an inverted crucible cover, and one drop of sulfuric acid (34.7 cc. of sulfuric acid to 35.6 cc. of water) was carefully added by means of a stirring rod to the edge of the cover so as to mix slowly with the acetic anhydride, when a characteristic fugitive violet color resulted if rosin was present.

Quantitative—From 2 to 10 g. of varnish were weighed into an Erlenmeyer flask—the size of the sample depending on the amount of rosin expected. It was saponified with a definite amount of 0.5 N alcoholic potash, usually 50 to 100 cc. A blank was run with 50 cc. of the potash. The alcohol was evaporated off and the residue dissolved in absolute alcohol and neutralized with 0.5 N acetic acid (glacial acetic in absolute alcohol). The blank was titrated to determine the amount needed for the neutralization.

Fifty cc. of petroleum ether (b. p. 40° to 60° C.) were added. After 15 min. water was added till the ether layer separated and the mixture was left in the ice box over night. It was next transferred to a separatory funnel to separate the aqueous and ether layers, the solid matter being left in the flask. The aqueous layer was washed with petroleum ether and the ether layer with water. The aqueous layers were discarded and the ether layers combined and washed with cold water until clear, transferred to an Erlenmeyer flask, and distilled. Twenty cc. of absolute alcohol (methyl alcohol may be used) and 20 cc. of a mixture of 1 part of concentrated sulfuric acid with 4 parts of absolute alcohol were added. After refluxing for 2 min., the mixture was transferred to a separatory funnel, the flask washed with ethyl ether, 200 cc. of a 10 per cent sodium chloride solution added, and the resin acids shaken out with 50 cc. portions of ethyl ether. The ether layer was washed with 10 per cent sodium chloride solution until free from mineral acid and transferred to a flask. Fifty cc. of neutral alcohol were added and the solution was titrated with 0.2 N potassium hydroxide, using phenolphthalein as an indicator. The results were calculated as follows:

$$\frac{\text{Cc. alkali} \times \text{factor} \times 0.0692}{\text{Wt. of sample}}\ 100 = \text{per cent of rosin}$$

We have found it convenient to use 0.5 N acid for our standard solution and to establish the ratio between it and the alkali before each titration of the acid from the rosin. In this way, when the amount of rosin was small we used 0.1 N and 0.05 N alkali solutions.

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[1] *Technologic Paper* 66

EXAMINATION OF FATTY ACIDS—Part of the acid obtained from the resin-oil separation was used to study the properties of the oils used in the manufacture of the varnish. The estimation of China wood oil was made according to the method given by the author,[1] and the calculations were based on the data given in the same article. Eisenschiml's hexabromide test[2] for fish oils was used for the detection of Menhaden oil.

DISCUSSION

The only seeming contradiction appears in the service test data, where some varnishes otherwise good show up badly. However, it will be noted that no varnish held up well on the north library doors, and if the results on these places are omitted, the results are in good agreement.

The relationships of the values for viscosity, sponge, surface, and elasticity to the service tests are apparent. These values for Nos. 1 and 3 are quite conclusive. The high rosin and resin-oil ratio in No. 11 suggest some limits, even if lack of more evidence prevents us from making it definite.

The complete results of tests and analyses on Nos. 11, 12, and 13 will be given in our next paper, along with the interior varnishes. The sample of No. 10 was too small for more tests, being a small sample sent in only for panel tests.

ACKNOWLEDGMENT

Many of the physical tests and some of the analytical work were performed under the author's direction by Mr. Vernon Ladd, an assistant in this department.

THE DETERIORATION OF CUBAN RAW SUGARS IN STORAGE

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Received January 29, 1920

The deterioration of manufactured sugars has been the subject of considerable investigation and has presented a number of interesting aspects, commercial as well as scientific. These have been considered in detail in another connection,[3] and it will suffice to state that many investigators have advanced evidence which proves that the loss in sucrose content which manufactured sugar undergoes on storage is due in a large measure to microbiological activities. It was in the hope of throwing some light on this phase of the problem that the following experiment was undertaken. While much valuable data may be found giving the analyses of sugars which have undergone deterioration, or those artificially inoculated for that purpose, there has not come to our notice any study based on the concomitant bacteriological and chemical analyses of sugar when stored under normal conditions, and which might be regarded as representative of large quantities of similarly stored sugar.

Two 320-lb. bags of each of three different "marks" of Cuban raw sugar representing an aggregate of approximately 5586 tons of sugar, were analyzed chemically and bacteriologically at the beginning of the storage period, and again in an identical manner at the end of 1 and 5.5 mo., respectively. Each bag was sampled as follows: A "long" trier was run in three places through the middle for the entire length of the bag. Two samples were drawn from each hole, and all mixed thoroughly on a sterile glazed paper, the composite being taken as representative of the contents of the middle of the bag. The usual precautions in bacteriological technique, against contamination of trier, mixing, etc., were observed by the use of alcohol. The bag was then skinned in two places; that is, the sugar at the surface just inside the bag was taken. Three samples were taken from each of these two holes, and after being thoroughly mixed were considered representative of the surface contents of the bag. All the holes thus made were immediately sewed up, except the hole always made by the official sampler with a short trier. These samples were analyzed chemically at once and a portion collected for bacteriological analysis in sterile containers. These were platted on Kopeloff's agar[1] in three dilutions. The averages given in the succeeding tables represent triplicate determinations of each dilution.

The bags were piled in 2 rows of 3 each (the lowest ones resting on the floor) and 2 burlap sacks thrown over the sides to approximate normal storage conditions as nearly as possible. Analyses were made at the end of 1, 4.25, and 5.5 mo., respectively.

A second series of bags was similarly obtained and analyzed the same way. These bags, however, represented only two marks—but were triplicate bags, one mark (G) being taken from the top of the vessel where the bags had been heated, the other mark (C) taken from the bottom of the vessel, two bags having been "stained" and another not "stained."

The chemical and bacteriological analyses of all samples are presented in Table I and summarized in Tables III and IV. Table II gives the conditions of humidity and temperature which obtained through this incubation period. Certain important generalizations may be deduced from the above data, among them the fact that there is a loss in polarization in all samples examined which were held for 5.5 mo. There is also a loss in polarization in practically all samples held one month or longer, and again in moisture content. The loss in polarization in each instance has generally been accompanied by a gain in reducing sugars, indicating that the loss is due to true inversion due to microbiological agencies. It will be remembered that Browne[2] has pointed out that "the average Cuban sugar of 96 per cent sucrose would deteriorate if stored in New York for one year to 95 and if stored in Cuba to 94 per cent sucrose," which calculated at 1916 prices would amount to $1,150,929. This large figure would have to be increased at current prices and production. From Tables I to III it will be seen in one case that there has been a loss of over 9.0 per cent, while there are three instances of a loss of more than 8.0 per cent.

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[1] This Journal, **11** (1919), 121.

[2] *Ibid.*, **2** (1910), 43.

[3] Louisiana Sugar Experiment Station, *Bulletin* **166**; This Journal, **12** (1920), 256.

[1] *Loc. cit.*

[2] This Journal, **10** (1918), 178.

TABLE I—CHEMICAL AND BACTERIOLOGICAL ANALYSES OF CUBAN RAW SUGARS IN STORAGE

NAME	Description	No.	Part of Bag	Date	Pol.	Loss in Pol.	Moisture Per cent	R. S. Per cent	Gain in in R. S. Per cent	Ash	Factor of Safety	No. Mic. per G.	Molds Per cent
B	Light	1	Mid.[1]	5/7	96.4	..	1.38	0.62	..	0.54	0.38	550	18
				6/10	97.0	..	1.07	0.63	0.01	..	0.36	200,000	*
				10/21	88.0	8.4	2.65	4.19	3.57	..	0.22	12,500	*
		1S	Sur.[2]	5/7	97.0	..	1.47	0.62	..	..	0.49	463	14
				6/10	96.8	0.2	1.15	0.76	0.06	..	0.36	2,500	*
				10/21	94.2	2.8	1.66	1.51	0.89	..	0.29	11,500	5
B	Dark	2	Mid.	5/7	93.8	..	1.88	1.26	..	0.80	0.30	480	6
				6/10	94.0	..	1.75	1.26	..	..	0.29	19,000	*
				10/21	93.9	..	1.80	1.12	..	..	0.30	4,250	7
		2S	Sur	5/7	93.5	..	2.10	1.49	..	..	0.32	1,034	2
				6/10	94.0	..	1.76	1.41	..	..	0.30	23,000	*
				10/21	92.5	1.0	2.54	1.84	0.35	..	0.34	17,250	2
M	Wet	3	Mid.	5/7	93.8	..	1.61	2.24	..	0.45	0.26	77,000	*
				6/10	93.0	0.8	1.44	2.84	0.60	..	0.21	19,000	*
				10/21	84.5	9.3	3.03	6.25	4.01	..	0.20	17,500	15
		3S	Sur.	5/7	96.9	..	1.10	0.78	..	..	0.36	4,305	*
				6/10	92.5	4.4	4.03	1.55	0.77	..	0.54	3,000	*
				10/21	88.0	8.9	2.92	5.69	4.91	..	0.24	7,250	4
	Average	4	Mid.	5/7	95.0	..	1.34	2.21	..	0.45	0.27	38,035	*
				6/10	94.4	0.6	1.08	2.53	0.32	..	0.20	50,000	*
				10/21	87.3	7.7	2.94	5.95	3.74	..	0.23	33,500	*
		4S	Sur.	5/7	96.9	..	0.94	0.80	..	..	0.30	4,018	1
				6/10	95.3	1.6	1.20	2.29	1.49	..	0.26	55,000	*
				10/21	91.3	5.6	2.25	3.76	2.96	..	0.26	8,500	*
U	Wet	5	Mid.	5/7	95.3	..	1.71	0.75	..	0.63	0.36	1,547	3
				6/10	95.0	0.3	1.31	1.23	0.48	..	0.26	1,700	*
				10/21	94.5	0.8	1.73	1.59	0.84	..	0.31	22,000	*
		5S	Sur.	5/7	95.8	..	1.45	1.22	..	..	0.35	251	12
				6/10	95.9	..	0.90	1.14	..	..	0.22	800	*
				10/21	90.5	5.3	2.81	3.71	1.49	..	0.30	11,500	*
	Average	6	Mid.	5/7	96.0	..	1.60	0.64	..	0.55	0.40	508	16
				6/10	96.0	..	1.20	1.02	0.58	..	0.30	20,500	*
				10/21	91.1	4.9	2.21	4.13	3.49	..	0.25	16,000	1
		6S	Sur.	5/7	96.8	..	1.16	0.61	..	..	0.36	1,040	3
				6/10	97.0	..	0.85	0.92	0.31	..	0.28	870	*
				10/21	89.8	7.0	3.00	5.55	4.94	..	0.30	8,000	*
G	Heated in top of vessel	7	Mid.	6/13	96.1	..	1.63	0.56	..	..	0.42	135	*
				10/21	93.8	2.3	1.85	2.53	1.97	..	0.30	350,000	*
		7S	Sur.	6/13	96.8	..	1.06	0.65	..	..	0.33	275	*
				10/21	90.3	6.5	2.75	4.19	3.54	..	0.28	80,000	*
		8	Mid.	6/13	96.2	..	1.74	0.58	..	..	0.46	285	*
				10/21	93.5	2.7	1.92	2.53	1.95	..	0.30	6,000	*
		8S	Sur.	6/13	95.9	..	1.24	1.23	..	..	0.30	170	*
				10/21	94.5	1.4	2.20	1.44	0.21	..	0.40	250,000	*
		9	Mid.	6/13	96.7	..	1.15	0.67	..	..	0.35	90	*
				10/21	93.2	3.5	1.88	2.53	1.86	..	0.27	5,500	*
		9S	Sur.	6/13	96.9	..	0.80	0.97	..	..	0.26	190	*
				10/21	88.5	8.4	3.40	6.25	5.28	..	0.30	8,500	*
C	Stained in bottom of vessel	10	Mid.	6/13	94.8	..	1.67	1.43	..	..	0.32	2,250	*
				10/21	94.5	0.3	1.60	1.70	0.27	..	0.29	25,000	*
		10S	Sur.	6/13	94.4	..	1.62	1.22	..	..	0.29	80,000	*
				10/21	94.0	0.4	2.71	2.08	0.86	..	0.45	135,000	*
		11	Mid.	6/13	95.8	..	1.23	1.46	..	..	0.30	80	*
				10/21	89.8	6.0	2.73	4.38	2.92	..	0.27	75,000	*
		11S	Sur.	6/13	96.6	..	1.00	1.02	..	..	0.23	550	*
				10/21	93.6	3.0	2.35	2.48	1.46	..	0.37	95,000	*
C	Not stained in bottom of vessel	12	Mid.	6/13	96.6	..	1.21	0.66	..	..	0.28	5,000	*
				10/21	94.0	2.6	1.89	1.96	1.30	..	0.32	75,500	*
		12S	Sur.	6/13	96.6	..	0.95	0.87	..	..	0.22	40,000	*
				10/21	94.0	2.6	2.07	1.70	0.83	..	0.35	135,000	*

[1] Mid. = Middle. [2] Sur. = Surface. * Negligible amount.

The economic importance of such data is too obvious to require amplification.

The total numbers of microörganisms responsible for this deterioration must needs vary considerably because of the difficulty in such an experiment of controlling the many variable factors which might have an influence on the microörganisms. However, it may be observed that in all bags heated in the top of the vessel during transit, or held in the bottom of the vessel, there was a decided increase in the number of microörganisms. As a rule the per cent of molds increased during the longer storage period, but not in one month. In general, there were more microörganisms in the middle than at the surface of the bag, as might readily be expected, since those at the periphery were more subject to a drying-out process. A correlation between numbers of microörganisms and deterioration was discernible where there was a heavy initial infection or a noteworthy rapid increase in the number of microörganisms. The factor of safety or moisture ratio, which is calculated by the formula

$$\text{M. R.} = \frac{\text{Moisture}}{100 - \text{Polarization}},$$

is in most instances over 0.35, in 6 of the instances 0.30 or more, in 4 of the instances over 0.27, and in the remaining 4 instances 0.22 or over. From the evidence advanced by other investigators it might be expected that practically all of these sugars are unsafe, although the general consensus of opinion seems to place the limit for the factor of safety at about 0.30. From the standpoint of mold infection it was found that even sugar with a lower factor of safety was unsafe, when sufficiently infected, and this would likewise seem to be the case where other microörganisms were concerned, as in the above instances, which represent about one-third of the samples under observation.

TABLE II—TEMPERATURE AND RELATIVE HUMIDITIES AT NEW ORLEANS, LA., MAY TO OCTOBER 1919

MONTH	Relative Humidity	Temperature ° F. Max.	Temperature ° F. Min.	Temperature ° F. Mean
May	75	85.04	64.00	74.52
June	77	88.00	69.00	78.10
July	77	91.00	71.80	81.40
August	79	91.50	72.90	82.22
September	67	88.10	68.10	78.10
October	76	90.00	67.00	88.50
AVERAGE	75	88.90	68.60	80.47

From the work done with molds it was concluded that with moisture ratios over 0.20, only 100 mold spores per gram were sufficient to cause deterioration. Since bacteria are, as a rule, somewhat smaller than mold spores it might be expected that a somewhat larger number of bacteria would be required to produce the same degree of deterioration. Therefore if there

Table III—Differences between Successive Samplings

Name	Description	Part	Date	Pol.	Moist.	R. S.	F. S.	Mic.	Molds
B	Light	Mid.	6/10	+	—	+	—	+	—
			10/21	—	+	+	—	—	+
		Sur.	6/10	—	—	+	—	+	—
			10/21	—	+	+	—	+	+
B	Dark	Mid.	6/10	(+)	—	+	(—)	+	—
			10/21	(—)	+	—	(+)	—	+
		Sur.	6/10	+	—	—	—	+	—
			10/21	—	+	+	+	—	+
M	Wet	Mid.	6/10	—	—	+	—	—	. .
			10/21	—	+	+	—	—	+
		Sur.	6/10	—	+	+	+	—	. .
			10/21	—	—	+	—	+	+
	Av.	Mid.	6/10	—	—	+	—	. .	. .
			10/21	—	+	+	+	+	—
		Sur.	6/10	—	+	+	—	—	. .
			10/21	—	+	+	. .	. .	. .
U	Wet	Mid.	6/10	—	—	+	—	+	—
			10/21	—	+	+	+	+	. .
		Sur.	6/10	—	—	—	—	+	—
			10/21	—	+	+	+	+	. .
	Av.	Mid.	6/10	. .	—	+	—	+	—
			10/21	—	+	+	—	—	+
		Sur.	6/10	+	—	+	—	—	—
			10/21	—	+	+	+	+	. .
G	Heated	Mid.	10/21	—	+	+	—	+	. .
		Sur.	10/21	—	+	+	—	+	. .
		Mid.	10/21	—	+	+	—	+	. .
		Sur.	10/21	—	+	+	+	+	. .
		Mid.	10/21	—	+	+	—	+	. .
		Sur.	10/21	—	+	+	+	+	. .
C	Heated	Mid	10/21	—	(—)	+	—	+	. .
		Sur.	10/21	—	+	+	+	+	. .
		Mid.	10/21	—	+	+	—	+	. .
		Sur.	10/21	—	+	+	+	+	. .
		Mid.	10/21	—	+	+	+	+	. .
		Sur.	10/21	—	+	+	+	+	. .
C	Moist	Mid.	10/21	—	+	+	+	+	. .
		Sur.	10/21	—	+	+	+	+	. .

+ Increase over previous sampling. — No increase over previous sampling. ( ) Questionable

were more than 100 bacteria at moisture ratios or factors of safety greater than 0.20, deterioration might be expected. That such is actually the case may be seen from Table IV, for here we find that deterioration occurs with factors of safety from 0.22 to 0.29, and the microörganisms responsible vary in number from 190 to 80,000 per gram. It is especially significant that the five largest numbers of microörganisms caused deterioration at factors of safety below 0.30. Browne[1] has shown that the explanation for this phenomenon is that the factor of safety becomes lower and consequently unreliable where deterioration is already in progress. This leads to an important commercial application; namely, next to eliminating deterioration it is of importance to predict the keeping quality of a sugar. It has been worked out empirically and scientifically that deterioration may be predicted[1,2] in sugars with a factor of safety greater than 0.30, and this is used as the basis for the next to last column of Table IV. In the final column, however, is included a prediction of deterioration based not on the factor of safety (for this is below 0.30) but on the number of microörganisms per gram. That is, with factors of safety above 0.20, upward of 100 microörganisms per gram would be expected to cause deterioration. While it is not possible to predict deterioration from the total number of microörganisms as confidently as in the case of mold infection, the parallel seems very striking and further experiments now in progress will form the basis for verification.

Table IV—Summary Showing Magnitude of Deterioration

No.	Name	Description	Part of Bag	Gain R. S. Per cent	Loss in Pol.	Factor of Safety	No. Micro. per G.	Deterioration Predicted from F. S.	Deterioration not Predicted from F. S. but from No. of Micro-organisms
9S	G	...	Sur.	5.28	8.4	0.26	190	—	+
6S	U	Av.	Sur.	4.94	7.0	0.36	1,040	+	. .
3S	M	Wet	Sur.	4.91	8.9	0.36	4,305	+	. .
3	M	Wet	Mid.	4.01	9.3	0.26	77,000	—	+
4	M	Av.	Mid.	3.74	7.7	0.27	38,035	—	+
1	B	Light	Mid.	3.57	8.4	0.38	550	+	. .
7S	G	...	Sur.	3.54	6.5	0.28	80,000	—	+
6	U	Av.	Mid.	3.49	4.9	0.40	508	+	. .
4S	M	Av.	Sur.	2.96	5.6	0.30	4,018	+	. .
11	C	St.	Mid.	2.92	6.0	0.30	80	+	. .
7	G	...	Mid.	1.97	2.3	0.42	135	+	. .
8	G	...	Mid.	1.95	2.7	0.46	285	+	. .
9	G	...	Mid.	1.86	3.5	0.35	90	+	. .
5S	U	Wet	Sur.	1.49	5.3	0.35	251	+	. .
11S	C	St.	Sur	1.46	3.0	0.23	550	—	+
12	C	Unst.	Mid.	1.30	2.6	0.28	5,000	—	+
1S	B	Light	Sur.	0.89	2.8	0.49	463	+	. .
10S	C	St.	Sur.	0.86	0.4	0.29	75,000	—	+
5	U	Wet	Mid.	0.84	0.8	0.36	1,547	+	. .
12S	C	Unst.	Sur.	0.83	2.6	0.22	40,000	—	+
2S	B	Dark	Sur.	0.35	1.0	0.32	1,034	+	. .
10	C	St.	Mid.	0.27	0.3	0.32	2,250	+	. .
8S	G	...	Mid.	0.21	1.4	0.30	170	+	. .
2	B	Dark	Mid.	..	...	0.30	480	+	. .

Table V—Sugars Ranked According to Deterioration

Order	Name	Most Deterioration by Bag	Most Deterioration in Bag	Least Deterioration by Bag	Least Deterioration in Bag
1	M	Wet	Surface	Average	Middle
2	G	....	Surface	....	Middle
3	U	Average	Surface	Wet	Surface
4	B	Light	Middle	Dark	Surface
5	C	Stained	(Surface) (Middle)	Unstained	(Middle) (Surface)

In Table V the sugars under investigation have been ranked in order of greatest deterioration. This ranking was arrived at by evaluation from the complete list in Table IV, and making the proper averages. In this way it is possible to tell at a glance that the greatest deterioration occurred in the "M" sugar, followed in order by "G," "U," "B," and "C." Similarly it is evident which of the duplicate bags (according to description) showed the most deterioration, and finally which part of that bag deteriorated to the greater extent. Because of the variety of sugars under consideration and the variation in composition, it is difficult to make many generalizations. It is interesting, however, to note that the "M" sugar which did not have a particularly high factor of safety and which deteriorated to the greatest extent, contained the largest number of microörganisms per gram (as may be seen from Table IV). A similar phenomenon is to be noted in the "C" sugar. On the other hand, "G," which was next in order of deterioration, had a comparatively high factor of safety and rather small number of microörganisms per gram. This would indicate again that deterioration is a resultant of these two variable factors. This fact to be observed in the "G" sugar is repeated in the case of the "U" and "B" sugars, which have relatively high factors of safety and not very high counts of microörganisms.

Considering the bag of each mark which showed the greatest deterioration, it is evident that those described as wet, stained, and light showed the greatest deterioration, as might be expected. The exception seems to be the "U average" which actually had a higher factor of safety than the so-called "wet" bag, and consequently might be expected to show greater deterioration, as was the case. When attention is turned to the part of each bag showing greatest deterioration, it is found in general that in the bags of each mark which had deteriorated to the greatest extent the surface shows most deterioration, while in the bags which have deteriorated least the middle of the bag seems to have been most affected. These results, as well as the fact that the factor of safety was found to decrease in every sample examined at the end of the incubation period, would appear to corroborate the very interesting report on deterioration of sugar in storage by Blake[1] as well as the investigations of Browne,[2] Owen,[2] and others already referred to.

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[1] *Loc. cit.*

[2] Louisiana Sugar Experiment Station, *Bulletin* **162**.

In general it was found that the deterioration was proportionally greater over the longer incubation period than at the end of one month, and this despite the fact that the total number of microörganisms per gram increased disproportionately the first month. In fact it would appear that rapid deterioration followed a rapid increase in the number of microörganisms. The authors are cognizant of the fact that any generalizations which have been made are limited by the small number of samples under consideration and apply only to the conditions of the experiment.

The foregoing investigation which is concerned with the chemical and bacteriological analyses of Cuban raw sugars under normal conditions of storage has served to bring out rather clearly the intimate correlation between the composition of a sugar and its microbiological content as influencing deterioration. In this way it becomes possible to modify the so-called "factor of safety rule" from the standpoint of microbiological infection and arrive at a satisfactory basis for predicting the keeping quality of sugar.

SUMMARY

I—Cuban raw sugars (with moisture ratios varying from 0.22 to 0.49) were stored under normal conditions for 5.5 mo. and analyzed chemically and bacteriologically. There was a loss in polarization at the end of this period, as well as at the end of one month, which was generally accompanied by a gain in reducing sugars. There was a gain in moisture content and reduction in the factor of safety.

II—There was a decided increase in total number of microörganisms after one month, which could be correlated within certain limitations with deterioration. Where there was a large initial infection, deterioration was rapid. In general there were more microorganisms in the middle of the bag than at the surface. The per cent of molds increased over the longer incubation period, but often failed to increase in one month.

III—A correlation between the number of microorganisms and the moisture ratio is indicated which appears to make it possible to predict the keeping quality of a sugar.

IV—Bags designated as wet, stained or having sugar light in color, deteriorated more rapidly than when drier, unstained, or dark in color. In bags of sugar which are deteriorating rapidly, the surface deterioration is greatest, while in less rapid deterioration the middle of the bag seems to undergo greater decomposition.

V—Deterioration was proportionately greater over a longer incubation period than in one month.

ACKNOWLEDGMENT

It is a privilege to acknowledge the invaluable assistance of Mr. J. McFetridge, whose interest made it possible to carry out this investigation, and the efficient help of Mr. Salvant and his associates in the American Sugar Refining Co., at Chalmette, La. We are indebted to Dr. C. A. Browne for his reading of the manuscript and constructive criticism.

JELLY

By C. H. Campbell

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Received December 13, 1919

Although jelly is a scientific product, it has never been considered as such by manufacturers. It should be so accurate scientifically that manufacturers can bring their raw materials together in the proper proportions and be sure to obtain a good, reliable commercial product.

To produce jelly, the proper proportions of acid, pectin and sugar are necessary. While much has been said as to the proper amounts of acid and sugar, nothing has ever come to the author's attention which demands a definite percentage of pectin as the fundamental basis for commercial jelly manufacturing. The following results prove that this is the only true basis.

It has been found that:

1—An excess of pectin produces a firm, tough jelly and decreases the amount. A pectin content of 1.25 per cent produces a fine commercial jelly; whereas, 1.0 or 0.75 per cent of pectin produces a delicate quality resembling homemade jelly.

2—An acidity of 0.3 per cent (as sulfuric acid) is necessary to produce a good quality, the minimum being 0.27 per cent and the maximum 0.5 per cent.

3—We know also that an excess of sugar produces a soft jelly, while an insufficient amount results in a tough product.

In an endeavor to determine the minimum amount of pectin necessary to produce jelly, several series of experiments were run, varying the per cent of pectin used but keeping the acidity and sugar constant. The following results were obtained:

SERIES I

	Original Apple Juice 1.22 Per cent Pectin	Diluted to 0.75 Per cent Pectin	Diluted to 0.5 Per cent Pectin
Volume, Gal.	1	1	1
Specific Gravity	1.017	1.010	1.005
Acidity (as H_2SO_4), Per cent	0.113	0.074	0.054
Sugar, per Gal.	3 lbs. 10 oz.	3 lbs. 10 oz.	3 lbs. 10 oz.
Acid (citric or tartaric) added,[1] grams	10	15	20
Cooked to ° F.	220	220	220
Yield, 8 oz. glasses	12	12.5	12
Quality	Firm, O. K.	Too soft for commercial use, but fine quality	

[1] Acid was added to juice to make acidity 0.3 per cent (as H_2SO_4) in each case.

SERIES II

	ORIGINAL JUICE	JUICE DILUTED TO			
Pectin, Per cent	1.695	1.3	1.0	0.75	0.5
Volume, Pint	1	1	1	1	1
Specific Gravity	1.038	1.025	1.020	1.016	1.012
Acidity (as H_2SO_4), Per cent	0.25	0.21	0.16	0.14	—
Sugar, Lb.	0.5	0.5	0.5	0.5	0.5
Acid added to bring per cent up to	0.25	0.3	0.3	0.3	0.34
Cooked to ° F.	222	221	222	222	222
Yield, 8 oz. glasses	1.5	1.5	1.5	1.5	1.5
Quality	Clear but dark	Fine, O. K.	Good	Good, too soft	Too soft

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[1] *Louisiana Planter*, **61** (1918), 316.

[2] *Loc. cit.*

SERIES III

	ORIGINAL JUICE	—JUICE DILUTED TO—	
Pectin, Per cent	1.62	1.0	0.75
Specific Gravity	1.020	1.017	1.012
Acidity, Per cent	0.118	0.073	...
Sugar, Lbs. per Gal	4.25	4.25	4.25
Acid added, grams	7	15	20
Cooked to ° F	221	221	221
Yield, 8 oz. glasses	13	13	13.5
Quality	Firm and stiff	Very good	Little soft

SERIES IV

	ORIGINAL JUICE	—JUICE DILUTED TO—				1 Per cent Pectin Base with Increased Sugar
Pectin, Per cent	1.59	1.25	1.0	0.75	0.5	...
Volume, Gal	1.5	1.5	1.5	1.5	1.5	1.5
Specific Gravity	1.017	1.012	1.008	1.007	1.006	1.017
Acidity, Per cent	0.25	0.21	0.176	0.132	0.113	0.25
Sugar added, Lbs	5 lbs. 1 oz.	5 lbs. 1 oz.	5 lbs. 1 oz.	5 lbs. 1 oz.	5 lbs. 1 oz.	8
Acid added, tsp[1]	1	1	1	1	1	1
Cooked to ° F	219	219	219	219	219	219
Yield, 8 oz. glasses	16	18	18.5	18	17	28
Quality	Very firm	Firm	Delicate	Soft	Soft	Good

[1] Teaspoonful acid (made by dissolving 1.5 lbs. acid per gal. water) added to each glass, rather than cooking with juice. Juice prepared by cooking pomace 2 hrs. with 0.5 oz. acid for each lb. pomace.

As the result of these tests special attention should be called to the fact that, regardless of the per cent of pectin in the juice used, the same amount of jelly was obtained.

The amount of sugar which would produce the best quality of jelly for commercial industries was next determined. A series of tests was run with various amounts of sugar per gallon of apple juice of a 1.25 per cent pectin content.

ANALYSIS OF JUICE

Specific Gravity	1.021
Acidity, Per cent	0.43
Pectin, Per cent	1.30

With this juice 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11 lbs. of sugar were used for each gallon of juice. The jelly became more delicate and sweeter as the amount of sugar increased. The lot containing 5 lbs. of sugar per gallon of juice was selected as best in texture for commercial use, but the lot containing 6 lbs. was considered best in flavor. The 9 to 11 lb. batches produced a fine, delicate jelly, which is more like home-made, but entirely too delicate for commercial use, and really too sweet to be relished.

Using as a base 1.25 per cent pectin with 5 lbs. of sugar per gallon, the following table which can be applied to an apple juice has been worked out:

SUGAR FOR APPLE JUICE—PECTIN BASE

Pectin Per cent	Sugar per Gallon of Apple Juice Lbs.	Oz.	Pectin Per cent	Sugar per Gallon of Apple Juice Lbs.	Oz.
0.50	2.0	..	1.25	5.0	..
0.60	2.0	6.4	1.30	5.0	3.2
0.70	2.0	12.8	1.40	5.0	9.6
0.80	3.0	3.2	1.50	6.0	..
0.90	3.0	9.6	1.60	6.0	6.4
1.00	4.0	..	1.70	6.0	12.8
1.10	4.0	6.4	1.80	7.0	3.2
1.20	4.0	12.8	1.90	7.0	9.6
			2.00	8.0	..
			2.50	10.0	..
			3.00	12.0	..

Since these results have been obtained, there has also been found a relationship between the Brix hydrometer reading of juice made from apple pomace and the amount of sugar to be added per gallon of juice. For every degree Brix, use a pound of sugar.

For example, if the juice reads 5.6° Brix, use 5.6 lbs. of sugar for every gallon. This will produce a fine, clear jelly, which is firm and will stand up under almost any climatic conditions. A more delicate jelly can be made by increasing the sugar to 1.25 lbs. per every degree Brix. The greater the amount of sugar the greater the yield.

QUANTITATIVE DETERMINATION OF PECTIN

The only test for pectin in use at present is the alcohol precipitation method where the pectin is precipitated with alcohol, dissolved in water, evaporated to dryness, dried, weighed, burned, and re-weighed, and the loss in weight expressed as pectin. Most methods call for a concentration of over 50 per cent alcohol in testing, but this is hardly sufficient as the sugars and other soluble substances are held in the concentrated mass of pectin precipitated.

The author used 10 cc. of filtered juice and 180 cc. of alcohol, adding the juice drop by drop from a pipette, with vigorous stirring. It was filtered immediately, dissolved in boiling distilled water, evaporated to dryness, heated 2 hrs. at 70° C. *in vacuo*, weighed, ashed, and re-weighed. The loss in weight multiplied by 10 equaled the per cent of pectin. It was not necessary to let the precipitate stand any length of time, as no further precipitate formed. The precipitate could be filtered through a Gooch crucible, thereby eliminating the dissolving and drying, often saving about 2 hrs. in handling.

A physical indication of the amount and quality of the pectin present in the juice may be obtained by observing the precipitation of the pectin as the juice is slowly run into the alcohol where the proportion of 10 cc. of juice to from 150 to 180 cc. alcohol is used. When the pectin amounts to over one per cent it will gather in a cohesive gummy mass, but if the amount is less, the precipitate is flocculent and will not gather in a solid mass. A little care in observing this precipitation will give a rough but quick check on the juice to be used.

The results obtained by using this quantitative method of determining pectin have been so concordant that they have been successfully applied to commercial jelly manufacturing, resulting in an increased production and an improved product. By thus controlling the manufacturing of jelly from a pectin standpoint it is possible to obtain a more uniform product than the average jelly manufacturer secures.

ACIDITY AND ACIDIMETRY OF SOILS. III—COMPARISON OF METHODS FOR DETERMINING LIME REQUIREMENTS OF SOILS WITH HYDROGEN ELECTRODE. IV—PROPOSED METHOD FOR DETERMINATION OF LIME REQUIREMENTS OF SOILS

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Received October 14, 1919

PART III

Through the courtesy of Mr. J. W. Ames of the Ohio Agricultural Experiment Station fifteen samples of soil were obtained from a number of variously treated plots from one of the fertility sections of the Wooster farm located on silt loam soil which is derived from sandstones and shales. Ames and Schollenberger[1] had made determinations of the lime requirement upon these soils by the Veitch, Hopkins, Hutchinson-MacLennan, MacIntire, and vacuum methods and all were tested with litmus paper and found to give a decided reaction. "The west half of the plots had been treated with 1,875 lbs. per acre of calcium oxide in 1903, and 2,000 lbs. of limestone in 1909. The composition of the lime materials applied was such that the equivalent of 5,700 lbs. of calcium carbonate had been applied to the limed halves of the plots previous to the time samples were taken from the plots, which was three years after the last treatment with lime."[2] The amount of lime left was negligible. All samples gave a decided acid reaction to litmus and when mixtures of the soils with recently boiled distilled water were tested with the hydrogen electrode all showed a hydrogen-ion concentration greater than 10^{-7}.

Hydrogen-ion concentrations were determined upon these soils by use of the hydrogen electrode, using 0.5 *N* potassium chloride solution containing various predetermined amounts of lime. The samples were shaken for 3 hrs. preceding the readings given in Table I.[3]

TABLE I—HYDROGEN-ION CONCENTRATIONS OF SOLUTIONS CONTAINING OHIO SOILS TO WHICH FIXED AMOUNTS OF LIME HAD BEEN ADDED
(Readings are given in volts)

PLOT	FERTILIZER	0 T. Lime	1 T. Lime	2 T. Lime	3 T. Lime	4 T. Lime
0	None	0.5174	0.5684	0.6300	0.6739	0.7450
	None. Lime	0.5670	0.6406	0.6850	0.7393	....
2	Acid Phosphate	0.5209	0.5725	0.6392	0.7000	....
	Acid Phosphate + Lime	0.5760	0.6561	0.6974	0.7473	....
5	Sodium Nitrate	0.5184	0.5671	0.6317	0.6862	0.7482
	Sodium Nitrate + Lime	0.5803	0.6511	0.7103	0.7540	....
11	Acid Phosphate + Mineral Potash + Sodium Nitrate	0.5164	0.5657	0.6308	0.6920	....
	Acid Phosphate + Mineral Potash + Sodium Nitrate + Lime	0.5626	0.6398	0.6865	0.7421	....
24	Acid Phosphate + Mineral Potash + Ammonium Sulfate + Lime	0.5445	0.6230	0.6612	0.7260	....
26	Bone Meal + Mineral Potash + Sodium Nitrate	0.5209	0.5731	0.6375	0.6774	0.7394
	Bone Meal + Mineral Potash + Sodium Nitrate + Lime	0.5516	0.6265	0.6841	0.7312	....
29	Basic Slag + Mineral Potash + Sodium Nitrate	0.5220	0.5794	0.6271	0.6826	0.7339
	Basic Slag + Mineral Potash + Sodium Nitrate + Lime	0.5668	0.6424	0.7074	0.7467	....
18	Manure	0.5202	0.5659	0.6164	0.6622	0.6938
	Manure + Lime	0.5574	0.6163	0.6708	0.7218	....

By interpolating the above results as straight line functions to determine the amount of lime necessary to lower the hydrogen-ion concentration to 10^{-7}, using 0.69 volt as the potential at this concentration, a comparison may be made directly with the results given by Ames and Schollenberger.[4] This comparison has been made in Table II. The results are given in pounds of lime as $CaCO_3$ required per acre.

The following conclusions may be drawn from a study of Table II:

1—The vacuum method approaches nearer to the lime requirement as shown by the hydrogen electrode than do any of the other methods, but with this method the results are uniformly higher. It may be assumed that if the soils had been shaken with the lime for a longer period than 3 hrs. the lime requirement as shown by the hydrogen electrode would have approached that given by the vacuum method.

2—It is quite evident that the above methods, with the possible exception of the vacuum method, do not indicate the amount of lime necessary to completely neutralize a soil, especially in the presence of neutral salts, except for a very limited period.

TABLE II—COMPARISON OF THE AMOUNTS OF LIME REQUIRED BY OHIO SOILS AS SHOWN BY VARIOUS METHODS

PLOT	FERTILIZER	Hopkins[1]	Veitch	MacIntire	Hutchinson	Vacuum	Hydrogen Electrode
1	None	3440	2000	3550	2925	7300	6456
	None. Lime	100	Alk.	2250	1700	4900	4225
2	Acid Phosphate	2640	2000	3850	2700	7800	5670
	Acid Phosphate + Lime	80	Alk.	2400	975	3800	3640
5	Sodium Nitrate	3640	1200	3550	2550	6200	6122
	Sodium Nitrate + Lime	120	Alk.	2500	1250	4225	3310
11	Acid Phosphate + Mineral Potash + Sodium Nitrate	3080	1800	3850	2825	7100	5960
	Acid Phosphate + Mineral Potash + Sodium Nitrate + Lime	80	Alk.	2500	1375	5900	4126
24	Acid Phosphate + Mineral Potash + Ammonium Sulfate + Lime	4240	3000	4000	2700	8300	4889
26	Bone Meal + Mineral Potash + Sodium Nitrate	2940	2000	3700	2250	7350	6407
	Bone Meal + Mineral Potash + Sodium Nitrate + Lime	360	Alk.	2900	1325	4050	4250
29	Basic Slag + Mineral Potash + Sodium Nitrate	2560	1200	3600	2250	6600	6288
	Basic Slag + Mineral Potash + Sodium Nitrate + Lime	150	Alk.	2100	1075	4050	3460
18	Manure	2760	2600	4200	3100	8500	7760
	Manure + Lime	120	Alk.	2950	1950	5200	4937

[1] Ohio Experiment Station, *Bulletin* **306** (1916), 350. Hopkins' values are given as one-half that given in the table here, for which no explanation is offered.

PART IV

The hydrogen electrode is not to be recommended for determination of the lime requirement of soils except as it may be valuable for checking other methods for the following reasons:

1—It is difficult to manipulate even by one who has had considerable experience in using it.

2—The process is slower than any method so far proposed.

3—Expensive and delicate apparatus is required if satisfactory results are to be obtained.

Although it may be found valuable for standardizing other methods, and approximate lime requirement values may be obtained by making two determinations and calculating the lime requirement as a linear function, the method cannot be taken seriously as a commercial laboratory method.

As the time element is an important factor automatic titration would not be entirely satisfactory. On account of the difficulties enumerated above, further investigations were made in the hope that a practical, rapid method for the determination of the lime requirement of a soil could be worked out.

Tacke's method[1] would appear to have a logical foundation but in the light of the present investigations it is difficult to conceive how it could be expected to yield concordant results, and it is doubtful if it or any of the proposed modifications would approach the actual amount of lime needed to bring the soil to true neutrality.

An attempt was made to determine the lime requirement by mixing a weighed quantity of soil with precipitated calcium carbonate, adding recently boiled distilled water, boiling for a fixed period, and determining the evolved carbon dioxide by the Parr method[1] as modified by Pettit.[2] Concordant results could not be obtained, but by adding a neutral salt rather close results were obtained.

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[1] THIS JOURNAL, **8** (1916), 243.

[2] *Ibid.*, **8** (1916), 224.

[3] For method and apparatus see Part II, *Ibid.*, **12** (1920), 457.

[4] *Ibid.*, **8** (1916), 244.

[1] *Chem.-Ztg.*, **20** (1897), 174.

The method used for the results given in Tables I and II below was to take a weighed sample of soil, usually 5 or 10 g., add an excess of precipitated calcium carbonate in a 125 cc. Erlenmeyer flask, attach to the Parr apparatus, run in about 25 cc. of normal salt solution,[3] and boil for a definite period.[4] The flask and condenser were filled with distilled water to a mark upon the capillary tube connecting the condenser with the eudiometer. Readings were taken as instructed by Pettit.[5] It is recommended that 10 min. be fixed as the time for boiling.

TABLE I—COMPARISON OF LIME REQUIREMENTS OF OHIO SOILS AS SHOWN BY VARIOUS METHODS, INCLUDING THE PROPOSED MODIFIED TACKE METHOD, AND THE DIFFERENCES SHOWN BY LIMED AND UNLIMED PLOTS. PREVIOUS APPLICATION OF LIME ON LIMED PLOTS 5700 LBS. PER ACRE

PLOT	FERTILIZER	Hopkins	Veitch	MacIntire	Hutchinson	Vacuum	Hydrogen Electrode	Modified Tacke 5 Min.	Modified Tacke Boiled 10 Min.
0	None	3440	2000	3550	2925	7300	6456	6941	7783
	None + Lime	100	Alk.	2250	1700	4900	4225	..	6908
	Difference	3340	..	1300	1225	2400	2231	..	875
2	Acid Phosphate	2640	2000	3850	2700	7800	5670	6737	7809
	Acid Phosphate + Lime	80	Alk.	2400	975	3800	3640	5123	6599
	Difference	2560	..	1450	1725	4000	2030	1644	1210
5	Sodium Nitrate	3640	1200	3550	2550	6200	6122	7264	7924
	Sodium Nitrate + Lime	120	Alk.	2500	1250	4225	3310	..	5431
	Difference	3520	..	1050	1300	1975	2812	..	2493
11	Acid Phosphate + Mineral Potash + Sodium Nitrate	3080	1800	3850	2825	7100	5960	7042	7493
	Acid Phosphate + Mineral Potash + Sodium Nitrate + Lime	80	Alk.	2500	1375	5900	4126	..	6184
	Difference	3000	..	1350	1450	1200	1834	..	1309
24	Acid Phosphate + Mineral Potash + Sodium Nitrate + Ammonium Sulfate + Lime	4240	3000	4000	2700	8300	4889	..	6547
26	Bone Meal + Mineral Potash + Sodium Nitrate	2940	2000	3700	2250	7350	6407	6973	7530
	Bone Meal + Mineral Potash + Sodium Nitrate + Lime	360	Alk.	2900	1325	4050	4250	..	6951
	Difference	2580	..	800	925	3300	2157	..	579
29	Basic Slag + Mineral Potash + Sodium Nitrate	2560	1200	3600	2250	6600	6288	..	7822
	Basic Slag + Mineral Potash + Sodium Nitrate + Lime	150	Alk.	2100	1075	4060	3460	..	6233
	Difference	2410	..	1500	1175	2540	2828	..	1589
18	Manure	2760	2600	4200	3100	8500	7760	8327	8776
	Manure + Lime	120	Alk.	2950	1950	5200	4937	..	7206
	Difference	2640	..	1250	1150	3300	2823	..	1570

The soils given in Table I are the ones described by Ames and Schollenberger[6] and received by the writer from them. The results are calculated in pounds of calcium carbonate to 2,000,000 lbs. of soil, except in case of peat soils where 1,000,000 lbs. were used as a basis.

Other soils investigated are given in Table II. Hopkins and hydrogen electrode determinations were made and the proposed modified Tacke determinations were made after boiling for 5, 10, and 30 min.

TABLE II—LIME REQUIREMENTS OF SOILS AS SHOWN BY THE HOPKINS, THE HYDROGEN ELECTRODE, AND THE PROPOSED MODIFIED TACKE METHODS[1]

			Proposed Modified Tacke Method		
SOILS	Hopkins	Hydrogen Electrode	5 Min.	10 Min.	30 Min.
Yellow-Gray Silt Loam	8400	12490	14847	15822	...
Black Peaty Loam	6890	32420	...	...	...
Black Clay Loam	9964	38026	...	34718	...
Peat	6535	34260	11011	20772	...
Black Muck	8112	(2)	...	31342	...
Yellow Silt Clay	10160	14708	...	...	...
Gray Clayey Silt	15840	(3)	28803	30640	33624
Gray Plastic Clay	5200	10000	...	11094	...
Yellow Plastic Clayey Silt	9340	14650	18173	19611	...
Yellow Silt Loam	5780	14578	13453	14954	17250
Brown Sandy Loam	3300	4574	...	5792	...

[1] For descriptions of soils see Part I, THIS JOURNAL, **12**, (1920), 340.

[2] More than 40000.

[3] More than 20000.

It will be noted that the proposed modification of Tacke's method gives varying results which depend upon the time of boiling, and in every case except for peat and yellow silt loam, Table II, the 5-min. boiling period showed a higher lime requirement than the hydrogen electrode. A 10-min. boiling period showed a higher lime requirement in every case except one (Ohio Plot No. 24, lime, Table I) than did the vacuum method proposed by Ames and Schollenberger.[1] That the reaction is not complete even at the end of the 10-min. period is shown by the increase at the end of a 30-min. boiling period.

The proposed method has the advantage over most of the others in that it gives a figure which represents the "power of a soil to decompose calcium carbonate" (which may be assumed to be a measure of the eventual lime absorption), is rapid, and approximates the results obtained with the hydrogen electrode.

It is quite apparent that the interaction at room temperature between a soil and a caustic lime solution containing a neutral salt is not complete within 3 hrs. (which is the period at which hydrogen-ion concentrations were determined with the hydrogen electrode), as shown by both the vacuum and the modified Tacke methods. The period required for the completion of the interaction at room temperature between a soil and calcium carbonate may be assumed to be considerable for MacIntire[2] has shown that calcium passes slowly into the form of silicates.

It is quite evident that any of the proposed methods gives comparative results only. The true lime hunger as it relates to cropping is after all the matter that we are most interested in determining, and this, it seems, with the present state of our knowledge must be determined by field experiments.

MEASUREMENT OF THE REDUCTION OF ACIDITY

By subtracting the acidity values found in acid soils from those found in unlimed soils from the corresponding half plots at the Ohio Station (Table I) differences are obtained which measure the residual reduction in acidity due to previous applications equivalent to 5,700 lbs. of calcium carbonate. As an average of the results from seven plots which afford data for this measurement the reduction in acidity is 2,864 lbs. by the Hopkins method, 2,674 by the vacuum method, and 2,388 by the hydrogen electrode, while the MacIntire, Hutchinson and modified Tacke methods show reductions of 1,243, 1,279, and 1,375 lbs., respectively. That any method will show a greater reduction in acidity than actually occurs and remains at the time of sampling seems extremely doubtful.

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[1] *J. Am. Chem. Soc.*, **26** (1904), 294.

[2] *Ibid.*, 1640.

[3] Preliminary experiments showed that it made little difference what neutral salt was used. Experiments were made with definite quantities of KCl, NaCl and KNO_3; also by varying the amount of calcium carbonate and KCl with duplicate results, provided there was an excess of calcium carbonate and not enough neutral salt to change materially the boiling point of the solution.

[4] If the boiling was attended with frothing a few drops of a neutral oil were added.

[5] *Loc. cit.*

[6] THIS JOURNAL, **8** (1916), 243.

[1] *Loc. cit.*, Part III.

[2] Tennessee Experiment Station, *Bulletin* **107** (1914).

As suggested above, the vacuum method appears to furnish the most trustworthy measure of the total lime requirement and it also seems safe to assume that the hydrogen electrode will give results in substantial agreement with the vacuum method if sufficient time is allowed. If these methods are accepted as standards, then the Hopkins method seems to give correct results when used to measure the reduction in soil acidity by applications of lime. It may also measure with accuracy the most immediate lime need, although it does not measure the total power of a soil to decompose carbonates.

If we assume that the reduction in acidity should be approximately the same for all limed plots, the Hopkins method and the hydrogen electrode show the highest percentage consistency.

CONCLUSIONS

1—A method has been proposed for determining the power of a soil to decompose calcium carbonate which approximates the results obtained by use of the hydrogen electrode.

2—The Hopkins and the hydrogen electrode methods show the highest percentage consistency for measuring the reduction of acidity for limed soils.

THE DETERMINATION OF ZIRCONIUM IN STEEL[1]

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Received November 3, 1919

I—INTRODUCTION

Any generally applicable method for the determination of zirconium in steels must make provision for a variety of elements which may be present as intentional or as accidental alloying constituents. Among such elements are titanium, aluminum, chromium, tungsten, vanadium, phosphorus, and, less commonly, uranium and cerium. Since zirconium steels very often contain aluminum and titanium, it is most desirable that any proposed method for the determination of zirconium should also provide for the determination of these analytically related elements in the same portion of steel. It is the purpose of this paper to give a critical review of the methods which have been published for this determination, to present methods which have been considered, and to describe a method which has been worked out at the Bureau of Standards. This method is not considered final and ideal, but it is the result of an effort to meet the requirements listed above.

II—HISTORICAL

KELLEY AND MEYERS[1] have described a method for the analysis of alloys of nickel and zirconium, which makes provision for silicon, tungsten, nickel, aluminum, zirconium, manganese, and small percentages of iron. Elements such as titanium and chromium were not encountered by the authors named, and therefore no provision was made for their separation and determination. Their method cannot be applied directly to the analysis of material high in iron, like zirconium steels.

FERGUSON METHODS—Ferguson[2] has given three optional methods for the determination of zirconium in steel. Abstracts of these methods are given with comments below.

Method I—The steel is dissolved in hydrochloric and nitric acids, the solution treated with sulfuric acid, evaporated to dryness, and the residue cooled and taken up in dilute sulfuric acid. The silica is filtered off, ignited, treated with sulfuric acid in excess, then with hydrofluoric acid; the solution is evaporated to the appearance of fumes, diluted and filtered. The filtrate is added to the previously obtained filtrate and the whole is nearly neutralized with ammonium hydroxide, treated with ammonium bisulfite and heated to boiling until the iron is reduced. The solution is cooled, made slightly alkaline with ammonium hydroxide, then slightly acid with hydrochloric acid, boiled, and precipitated with phenylhydrazine. After digestion, the precipitate is filtered off, dissolved in hydrochloric acid, reprecipitated with phenylhydrazine after ammonium bisulfite reduction, filtered, washed, ignited, and weighed. The ignited oxides are fused with sodium carbonate, the melt is treated with water, and aluminum separated by treatment with sodium hydroxide followed by filtration. The insoluble residue is ignited and fused with potassium pyrosulfate; the melt is dissolved in water, and the zirconium precipitated with ammonium hydroxide if iron is absent, or with phenylhydrazine after reduction when iron is present; the precipitate is filtered and ignited to zirconium oxide.

This method, if we grant quantitative separations, is still open to the following objections:

1—No provision is made for titanium, which is a common constituent of zirconium steels and which will accompany the latter through all the separations and finally be counted as zirconium oxide.

2—No provision is made for chromium, which is a possible contaminant of zirconium steels and which will be counted as aluminum in this method if the carbonate fusion takes place in an oxidizing atmosphere, and as zirconium if the atmosphere is reducing.

3—Phosphorus in the steel will be present as phosphorus pentoxide in the phenylhydrazine precipitate and will be reckoned finally as aluminum.

4—Cerium, uranium, and vanadium will also cause complications, the cerium being counted as zirconium, while vanadium and uranium will go with the aluminum.

Method II—In this method Ferguson proceeds as in Method I until the reduced iron solution has been rendered slightly alkaline. At this point the solution is treated with 2 cc. of concentrated sulfuric acid, diluted to 400 cc., and disodium phosphate added. After boiling and digestion, the precipitate is filtered off, washed with one per cent sulfuric acid, then with hot water, ignited, blasted, and weighed as zirconium phosphate, for which the zirconium factor 0.3828 is given.

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[1] Published by permission of the Director of the Bureau of Standards.

[1] This Journal, 9 (1917), 854.

[2] *Eng. Mining*, 106 (1918), 793.

This method is open to the following objections:

1—The zirconium phosphate which is finally weighed is of indefinite composition and consequently no true zirconium factor can be given.[1]

2—No provision is made for titanium, which will certainly contaminate the zirconium phosphate if hydrogen peroxide is not added before the phosphate precipitant.

3—Aluminum, chromium, and iron, if present, will contaminate a zirconium phosphate thrown out in such low acidity (one per cent by weight), as shown by Nicolardot and Reglade.[2]

4—No provision is made for the determination of titanium and aluminum.

Method III—In this method Ferguson takes the combined aluminum and zirconium hydroxide from the second phenylhydrazine precipitation, dissolves them in 40 cc. of hot 1 : 1 hydrochloric acid, dilutes to 100 cc., cools, and precipitates with a cold 6 per cent water solution of cupferron. The precipitate is washed in succession with cold dilute hydrochloric acid, water, ammonium hydroxide, and again with water, and ignited to zirconium oxide.

This method is open to the following objections:

1—No provision is made for titanium, which is therefore counted as zirconium.

2—Cupferron precipitates iron and consequently the second phenylhydrazine precipitate must be absolutely free from iron.

3—Vanadium, cerium, and uranium would probably cause contamination of the final precipitate.

4—No provision is made for the determination of aluminum.

JOHNSON'S METHOD—Johnson's[3] method for the determination of zirconium in steels is as follows:

The steel is dissolved in sulfuric acid with minimum oxidation; the residue is filtered off, ignited, and treated with hydrofluoric and sulfuric acids; the solution is evaporated till white fumes escape and added to the main solution, which is then treated with ammonium hydroxide until the first appearance of a black precipitate. The precipitate containing zirconium and aluminum, together with a little iron, is filtered and dissolved in hydrochloric acid; the solution is ozidized with sodium peroxide, boiled with sodium carbonate, and filtered. Most of the aluminum is thus separated from iron and zirconium. The remainder is separated by a second treatment. Aluminum is recovered from the filtrates by adding hydrochloric acid until the solution is no longer alkaline to turmeric, filtering off the aluminum hydroxide, dissolving in acid, and reprecipitating with ammonium hydroxide. The sodium peroxide-carbonate precipitate containing iron and zirconium is dissolved in sulfuric acid, and treated with disodium phosphate and then ammonium hydroxide until a precipitate starts to form. After digestion, the mixture of zirconium and iron phosphates plus some silica is filtered, washed with water, ignited and treated with hydrofluoric and sulfuric acids; the acids are evaporated till white fumes appear, the residue washed into a beaker, warmed to dissolve ferric sulfate, filtered, and the residue ignited to "zirconium phosphate," for which the zirconium factor 0.3838 is given.

Johnson's method is open to the following objections:

1—The zirconium value cannot be correct except through a most fortunate balancing of errors. Washing of zirconium phosphate with water causes hydrolysis with formation of a basic phosphate of indefinite composition.

2—The prescribed treatment of the impure basic phosphate results in further loss of phosphoric acid, and no definite composition can be ascribed to the ignited residue.

3—No provision is made for the determination or the interference of titanium which is a frequent constituent of zirconium steels.

TRAVERS' METHOD—Travers'[1] method for the determination of zirconium in steel is as follows:

Silicon is first eliminated and then the greater part of the iron by an ether separation. After boiling out the ether, a double precipitation is made by Chancel's[2] sodium thiosulfate method. The precipitate is ignited, fused with potassium carbonate, extracted with water and the aluminum determined in the filtrate. The residue is dissolved in hydrochloric and nitric acids (any insoluble matter being fused and recovered), and the solution again treated by Chancel's method. The resulting precipitate is ignited, and weighed as ZrO_2 plus TiO_2. It is then fused with potassium pyrosulfate and the melt taken up with water; to the solution is added an excess of hydrogen peroxide, the precipitate formed is filtered off, and ignited to ZrO_2, while TiO_2 is determined colorimetrically in the filtrate.

Travers' method is open to the following objections:

1—No provision is made for such possible interfering elements as chromium, tungsten, vanadium, and phosphorus.

2—No experimental data are given which might cast light on the sharpness of the separations, particularly the separation of zirconium from titanium by precipitation with hydrogen peroxide in dilute sulfuric acid solution.

III—SEPARATIONS CONSIDERED BEFORE ADOPTION OF BUREAU OF STANDARDS METHOD

(1) HILLEBRAND'S[3] METHOD OF PRECIPITATING ZIRCONIUM AS PHOSPHATE IN H_2SO_4-H_2O_2 SOLUTION—Nicolardot and Reglade[4] have shown that a solution must contain 20 per cent by weight of sulfuric acid in order to prevent contamination of zirconium phosphate by ferric phosphate. Experiments upon solutions of steels treated with known amounts of zirconium, titanium, and aluminum as shown in Table I demonstrated that this method is not reliable for such materials, even though the weighed phosphate is analyzed for its contaminants. This method has the additional disadvantage that it requires separate determinations of aluminum and titanium. It may serve for the qualitative detection of zirconium in 5-g. portions of steel when this element is present in amounts over one-tenth of one per cent.

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[1] G. E. F. Lundell and H. B. Knowles, *J. Am. Chem. Soc.*, **41** (1919), 1801.

[2] *Compt. Rend.*, **168** (1919), 350.

[3] *Chem. & Met. Eng.*, **20** (1919), 588.

[1] *Chim. et Ind.*, **2** (1919), 385.

[2] *Compt. Rend.*, **46** (1858), 987.

[3] U. S. Geol. Survey, *Bulletin* 148, and subsequent editions.

[4] *Compt. Rend.*, **168** (1919), 348.

TABLE I

(Steel taken, 5 g. Precipitating conditions: 300 cc. total volume, 20 per cent sulfuric acid (sp gr. 1.84) by weight, 20 cc. hydrogen peroxide, 5 per cent ammonium nitrate wash water)

Expt. No.	Time of Digestion	Zr Present	Ti Present	Al Present	Wt. of Impure Phosphate	Ti in Impure Phosphate	Fe in Impure Phosphate	Zr Found (Diff.)	Error
	Hrs.	G.	G.	G.	G.	G.	G.	G.	G.
1	2	0.0500	0.0480	0.0500	0.1641	0.0005	0.0197	0.0366	—0.0134
2	18	0.0500	0.0480	0.0500	0.1641	0.0006	0.0079	0.0480	—0.0020
3	2	0.0099	0.0100	0.0099	0.0172	..	..	0.0059[1]	—0.0040
4	18	0.0099	0.0100	0.0099	0.0168	..	..	0.0058[1]	—0.0041

[1] Represents Zr calculated upon the assumption that the precipitate was pure zirconium phosphate.

(2) DIRECT PRECIPITATION OF ZIRCONIUM PHOSPHATE IN H_2SO_4 SOLUTION WITH ALL OF THE IRON IN FERROUS CONDITION—This method was not studied because of the following apparent drawbacks:

(*a*) If precipitation of zirconium as phosphate is complete, the precipitate will certainly be contaminated by titanium and probably also by iron.

(*b*) The determination of aluminum and titanium would require new portions of material and the development of separate methods of analysis.

(3) BAILEY'S[1] METHOD FOR SEPARATING ZIRCONIUM FROM IRON, ALUMINUM, AND TITANIUM IN WEAK H_2SO_4 SOLUTION BY MEANS OF EXCESS H_2O_2—Hillebrand[2] found that the complete precipitation of zirconium in dilute sulfuric acid solution by means of ordinary hydrogen peroxide is impossible. A like observation has been made by Piccini.[3] Even though complete precipitation is possible with a stronger reagent like perhydrol, it does not appear likely that a clear-cut separation of zirconium from iron and other elements can be had by this method. It has also the disadvantages mentioned in (*b*) above under (2).

(4) VOLATILIZATION OF IRON FROM A MIXTURE OF OXIDES IN A CURRENT OF CHLORINE AND HCl GAS[4]—As pointed out by Travers,[5] the volatilization of iron is attended with considerable difficulty and the danger of volatilizing zirconium increases as the temperature is raised above 650° C. It is also evident that this treatment would be only a preliminary separation.

(5) BASKERVILLE'S[6] METHOD OF PRECIPITATING TITANIUM AND ZIRCONIUM BY BOILING WITH H_2SO_3 AND A VERY WEAK HCl SOLUTION OF THE CHLORIDES—This method seemed quite attractive but it was found that:

(*a*) The correct neutralization of the reduced acid solution of steel is a very difficult matter. Excess acidity causes low values, low acidity results in high contamination.

(*b*) The complete elimination of aluminum, iron, and phosphorus presents difficulties.

(*c*) In addition to the above drawbacks, the presence of chromium, cerium, and vanadium would undoubtedly cause inconvenience, and the determination of aluminum would require a special procedure.

(6) MATTHEWS'[1] METHOD FOR SEPARATION OF ZIRCONIUM FROM IRON BY TREATMENT OF DRY CHLORIDES WITH ANHYDROUS ETHER SATURATED WITH HCl GAS—Aside from practical objections to the method, such as the specification of absolute ether saturated with hydrochloric acid gas, it is not satisfactory since the precipitate will contain zirconium, titanium, aluminum, chromium, cerium, and possibly phosphorus and vanadium. It is obvious that this would be but a start in the analysis of the steel.

(7) REDUCTION OF IRON AS IN FERGUSON'S METHOD FOLLOWED BY PHENYLHYDRAZINE PRECIPITATION[2]—The following drawbacks are apparent:

(*a*) Difficulty in removing all iron.

(*b*) The phenylhydrazine precipitate will contain in addition to possible iron, all of the zirconium, titanium, aluminum, chromium, cerium, and phosphorus, probably all uranium, and considerable vanadium.

(*c*) The analysis of the above complex mixture would require very careful analytical procedures.

(8) SIMILAR TO ABOVE METHOD WITH FINAL SOLUTION OF PHENYLHYDRAZINE PRECIPITATE AND PRECIPITATION WITH CUPFERRON—In this procedure the following troubles were anticipated:

(*a*) The necessity for removing all iron in the preliminary phenylhydrazine precipitations.

(*b*) The question as to whether phenylhydrazine would interfere in a cupferron precipitation.

(*c*) The necessity of destroying organic matter before the precipitation of aluminum, and the interference of phosphorus in its determination; as well as the interference of other constituents such as chromium, vanadium, cerium, and uranium.

(9) STROMEYER'S[3] APPLICATION OF CHANCEL'S[4] METHOD OF SEPARATING IRON FROM ALUMINUM AND ZIRCONIUM BY PRECIPITATION WITH SODIUM THIOSULFATE IN WEAK HCl SOLUTION—Hermann's[5] statement that it is difficult to separate all iron by this method, and the fact that the precipitates may be expected to contain a variety of elements such as aluminum, chromium, cerium, etc., led us to avoid this procedure.

(10) BERLIN'S[6] METHOD IN WHICH MIXED OXIDES OF IRON AND ZIRCONIUM ARE FUSED WITH SODIUM CARBONATE AT WHITE HEAT, AND THEN TREATED WITH HCl, WHICH DISSOLVES IRON AND LEAVES ZIRCONIUM UNATTACKED—Scheerer's[7] statement concerning the incompleteness of the separation and the partial solution of the zirconium, taken together with obvious difficulties on account of the large amount of iron to be dealt with, led us to table this procedure.

(11) DITTRICH AND FREUND'S[8] METHOD OF SEPARATING ZIRCONIUM AND TITANIUM FROM IRON IN BIVALENT CONDITION BY PRECIPITATION WITH SODIUM ACETATE—It is obvious that the sodium acetate pre-

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[1] *J. Chem. Soc.*, **49** (1886), 149, 481.

[2] Private communication.

[3] *Gazz. chim. ital.*, **17** (1887), 479.

[4] F. S. Havens and A. F. Way, *Am. J. Sci.*, **8** (1899), 217.

[5] *Loc. cit.*

[6] *J. Am. Chem. Soc.*, **16** (1894), 475.

[1] *J. Am. Chem. Soc.*, **20** (1898), 846.

[2] E. T. Allen, *Ibid.*, **25** (1903), 421.

[3] *Ann. Chem. Pharm.*, **113** (1860), 127.

[4] *J. prakt. Chem.*, **74** (1858), 471.

[5] *Ibid.*, **97** (1866), 337.

[6] *Ibid.*, **58** (1853), 145.

[7] *Pogg. Ann.*, **59** (1843), 481.

[8] *Z. anorg. Chem.*, **56** (1907), 348.

cipitate will carry down in addition to zirconium and titanium such elements as aluminum, chromium, phosphorus, and probably more or less vanadium, and that the use of this reagent would therefore be but a preliminary step in the analysis.

(12) ELECTROLYSIS WITH MERCURY CATHODE OF DILUTE ACID SOLUTIONS OF THE STEEL CONSTITUENTS[1]—By this method iron, cobalt, nickel, copper, and chromium can be deposited and separated from such elements as aluminum, zirconium, titanium, uranium, cerium, thorium, manganese, phosphorus, and vanadium. Such a separation would obviously be most desirable in a plain zirconium steel; in this case a subsequent separation of zirconium from manganese and phosphorus would be required. In more complex alloys, the electrolysis would serve only as a preliminary separation, and it is doubtful whether the operations incidental to the preparation of the solution for electrolysis and the electrolysis set-up would entail any less time and labor than an ether separation or a separation by Johnson's method.[2]

IV—BUREAU OF STANDARDS METHOD

(A) PRELIMINARY STATEMENT

The method developed at the Bureau of Standards permits the determination of silicon, aluminum, titanium, and zirconium in one portion of the steel, and provides for the following possible interfering elements: tungsten, chromium, uranium, cerium, manganese, phosphorus, vanadium, molybdenum, copper, nickel, and cobalt.

(B) METHOD

Dissolve 5.00 g. of the steel in 50 cc. of hydrochloric acid (sp. gr. 1.2) with gentle warming and the addition of one cc. portions of nitric acid from time to time to insure solution of the zirconium and titanium and also oxidation of the iron.

When solution is complete, evaporate to dryness, take up in 10 cc. of hydrochloric acid (sp. gr. 1.2), again evaporate to dryness, and finally bake at a gentle heat in order to decompose nitrates. Cool, take up in 50 cc. of 1 : 1 hydrochloric acid, and filter when the iron is completely in solution. Wash the residue with hot 3 per cent hydrochloric acid. Save the filtrate and washings.

Ignite the residue and paper in a platinum crucible, cool, and weigh. Treat with 1 cc. of sulfuric acid (1 : 1) and sufficient hydrofluoric acid, fume off in the usual manner, ignite and weigh to obtain silica, and calculate silicon. Fuse the slight residue left after the hydrofluoric acid treatment with a small amount of potassium pyrosulfate, dissolve in 10 to 20 cc. of 5 per cent sulfuric acid and add the solution to the acid extract from the ether separation obtained as described below.

Evaporate the filtrate and washings from the silica determination to a sirupy consistency, take up in 40 cc. of hydrochloric acid (sp. gr. 1.1) and extract with ether in the usual manner. (The ether extract will contain most of the molybdenum, and this element may be qualitatively tested for in it. If molybdenum is present it is more conveniently determined in a separate portion of steel.) The acid extract will contain some iron, and all of the zirconium, titanium, aluminum, nickel, chromium, etc.

Gently boil off the ether in the acid extract, add the matter recovered from the silica, oxidize ferrous iron with a little nitric acid, dilute to 300 cc., cool, and precipitate with 20 per cent sodium hydroxide solution, adding 10 cc. in excess. The sodium hydroxide solution should be as pure as possible and free from carbonate. Filter, and save the filtrate. Dissolve the precipitate in warm dilute 1 : 1 hydrochloric acid, repeat the sodium hydroxide precipitation, filter, and combine the sodium hydroxide filtrates. Dissolve the sodium hydroxide precipitate in warm dilute 1 : 1 hydrochloric acid and reserve the solution for subsequent analysis.

It is advisable to treat as follows the filter or filters used above: Ignite in platinum, fuse with sodium carbonate, digest the cooled melt with hot water, wash the residue, discard the filtrate and washings, dissolve the residue in hot 1 : 1 hydrochloric acid and add to the main acid solution. This precaution makes certain the recovery of any zirconium held back on the filter as zirconium phosphate insoluble in acid.

DETERMINATION OF ALUMINUM. (*a*) *In the Absence of Chromium and Uranium*—Add a few drops of methyl red to the sodium hydroxide filtrate, neutralize with hydrochloric acid, add 4 cc. of concentrated hydrochloric acid per 100 cc. of solution, boil, make barely alkaline with ammonium hydroxide, continue the boiling for 3 min., and set the beaker aside for 10 min. If no precipitate settles out, the absence of aluminum is assured. If a white precipitate settles out, aluminum is indicated. This precipitate is always contaminated by phosphorus pentoxide and must be purified as follows: Filter without washing, discard the filtrate and dissolve the precipitate in warm 1 : 1 hydrochloric acid. Dilute the solution to 50 cc., make alkaline with ammonium hydroxide, neutralize with nitric acid and add 2 cc. in excess. Warm to 50° C., precipitate the phosphoric acid with molybdate reagent in the usual manner, filter, and wash the phosphomolybdate with an ammonium acid sulfate solution. Precipitate the aluminum in the filtrate as directed above, filter without washing, dissolve the precipitate in warm 1 : 1 hydrochloric acid, reprecipitate, filter, wash slightly with 2 per cent ammonium chloride solution and ignite in a platinum crucible. The ignited residue is usually contaminated by silica, therefore a sulfuric acid-hydrofluoric acid treatment followed by ignition to alumina over the blast lamp should be performed. (The sodium hydroxide reagent must be tested for substances precipitable by ammonia, and appropriate corrections must be made in the aluminum determination when these are present.)

(*b*) *In Steels Containing Chromium*—Proceed as above until the filtrate from the molybdate precipitation is obtained. Then make the solution ammoniacal, oxidize with a little bromine water, make just acid with 1 : 2 nitric acid, add ammonium hydroxide in slight excess, heat to boiling, filter, dissolve the precipitate in dilute hydrochloric acid, and reprecipitate the aluminum hydroxide as directed above.

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[1] Wolcott Gibbs, *Am. Chem. J.*, 13 (1891), 570; Edgar F. Smith, "Electro-Analysis," 5th Ed., p 256; T. M. Drown and A. McKenna, *Trans. Am. Inst. Mining Eng.*, 20 (1891), 242; J. R. Cain, THIS JOURNAL, 3 (1911), 476.

[2] *Loc. cit.*

(*c*) *In Steels Containing Uranium*—The only modification which is required is the substitution of ammonium carbonate for ammonium hydroxide as the final precipitant of the aluminum hydroxide.

(*d*) *In Steels Containing Vanadium*—Alumina which is obtained by the above procedures from steels containing vanadium is contaminated by this element. When dealing with these steels proceed as follows: Fuse the weighed residue with pyrosulfate, extract the cooled melt with 5 per cent sulfuric acid, reduce the vanadium in a Jones reductor having ferric alum in the receiver, titrate the reduced solution with standard permanganate, calculate the vanadium as V_2O_5 and subtract from the original weight.

DETERMINATION OF ZIRCONIUM AND TITANIUM—Dilute the hydrochloric acid solution to 250 cc., neutralize with ammonium hydroxide so as to leave approximately 5 per cent (by volume) of hydrochloric acid, add 2 g. of tartaric acid, and treat with hydrogen sulfide until the iron has been reduced. Filter if the sulfide group is indicated. Make the hydrogen sulfide solution ammoniacal and continue the addition of the gas for 5 min. Filter carefully and wash with dilute ammonium sulfide-ammonium chloride solution. Filter through a new filter if the presence of iron sulfide in the filtrate is indicated. Save the filtrate.

(The sulfide precipitate consists of ferrous sulfide, in addition to the greater part of any nickel, cobalt and manganese present in steel. It is preferable to determine these in separate portions of the steel.)

Neutralize the ammonium sulfide filtrate with sulfuric acid, add 30 cc. in excess and dilute with water to 300 cc. Digest on the steam bath until sulfur and sulfides have coagulated, filter, wash with 100 cc. of 10 per cent sulfuric acid, and cool the filtrate in ice water.

Add slowly and with stirring an excess of a cold 6 per cent water solution of cupferron. (The presence of an excess is shown by the appearance of a white cloud which disappears, instead of a permanent coagulated precipitate.) After 10 min. filter on paper, using a cone and very gentle suction, and wash the precipitate thoroughly with cold 10 per cent hydrochloric acid.

Carefully ignite in a tared platinum crucible, completing the ignition over a blast lamp or large Meker burner, cool, and weigh the combined zirconium and titanium oxides.

Fuse with potassium pyrosulfate, dissolve in 50 cc. of 10 per cent (by volume) sulfuric acid and determine titanium colorimetrically or volumetrically. Calculate titanium oxide, subtract the weight found from that of the combined oxides, and calculate zirconium.

(C) NOTES ON THIS METHOD

1—Phosphorus pentoxide contaminates the precipitate to so slight an extent that it can be disregarded.

2—Vanadium interferes no matter what its valency. The interference is not quantitative. If present in the steel, proceed as usual through the weighing of the cupferron precipitate. Then fuse thoroughly with sodium carbonate, cool, extract with water, filter, and determine the vanadium in the filtrate by adding sulfuric acid, reducing through a Jones reductor into a solution of ferric alum-phosphoric acid and then titrating with standard permanganate. Vanadium is thus reduced to V_2O_2 and then oxidized to V_2O_5. Calculate V_2O_5 and subtract from the combined oxides. Ignite in the original crucible the matter insoluble in water, fuse with potassium pyrosulfate and proceed as directed for titanium.

3—Tungsten does not interfere since it is separated from zirconium and titanium by the sodium hydroxide treatment, and from aluminum by the ammonium hydroxide precipitation. If tungsten is present in large amount it may be found desirable to fuse the nonvolatile residue from the silicon determination with sodium carbonate, extract with water, filter, dissolve the residue in hot 1 : 1 hydrochloric acid, and add to the acid extract from the ether separation.

4—Uranium is partially carried down when present in the quadrivalent condition, but not at all in the sexivalent state. If this element is suspected, boil out all hydrogen sulfide before the cupferron precipitation, oxidize with permanganate to a faint pink, cool, and proceed with the cupferron precipitation.

5—Thorium and cerium interfere, but they are not thrown down quantitatively. In case these elements are suspected, the peroxidized solution used for the titanium determination must be quantitatively preserved and reduced with a little sulfurous acid. The rare earths are then separated by Hillebrand's method[1] as follows: Precipitate the hydroxides with an excess of potassium hydroxide, decant the liquid, wash with water once or twice by decantation and then slightly on the filter. Wash the precipitate from the paper into a small platinum dish, treat with hydrofluoric acid, and evaporate nearly to dryness. Take up in 5 cc. of 5 per cent (by volume) hydrofluoric acid. If no precipitate is visible, rare earths are absent. If a precipitate is present, collect it on a small filter held by a perforated platinum or rubber cone and wash it with from 5 to 10 cc. of the same acid. Wash the crude rare-earth fluorides into a small platinum dish, burn the paper in platinum, add the ash to the fluorides and evaporate to dryness with a little sulfuric acid. Dissolve the sulfates in dilute hydrochloric acid, precipitate the rare-earth hydroxides by ammonia, filter, redissolve in hydrochloric acid, evaporate the solution to dryness, and treat the residue with 5 cc. of boiling hot 5 per cent oxalic acid. Filter after 15 min., collect the oxalates on a small filter, wash with not more than 20 cc. of cold 5 per cent oxalic acid, ignite and weigh as rare-earth oxides which are to be deducted from the weight of the cupferron precipitate.

The above procedure does not give an absolutely quantitative recovery of the rare earths. Experiments indicate a recovery of approximately 85 per cent of the rare earths present in residues containing 100 mg. of zirconia, 2 mg. of thoria, and 2 mg. of ceria. Attempts which were made to omit the preliminary separation of the rare earths, as fluorides, were unsuccessful.

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[1] U. S. Geol. Survey, *Bulletin* 700, 176.

6—Instead of the prescribed treatment for the removal of the bulk of the iron, Johnson's[1] method of fractional precipitation with ammonium hydroxide may be used. When using this method, it is recommended that the 1 : 1 hydrochloric acid solution of the ammonium hydroxide precipitate should be further treated as given in the Bureau of Standards method beginning with "oxidize........and precipitate with a 20 per cent sodium hydroxide solution." In Johnson's procedure silicon must be determined in a separate portion.

7—After considering the method and studying the notes, the reader might ask the question, "Why not use ammonium hydroxide instead of cupferron as the final precipitant?" The disadvantages of such a procedure are the following:

(*a*) The necessity for destroying the tartaric acid which is in the solution, with attendant danger of contamination by material resulting from the attack on glassware; (*b*) the co-precipitation of phosphorus and also chromium and uranium when they are present.

The advantages of an ammonia precipitation are: (*a*) It is a cheaper reagent; (*b*) the precipitation of cerium would be complete instead of partial.

The following scheme of analysis is now being tested at this Bureau: Zirconium, titanium, aluminum, cerium, chromium, vanadium, etc., are first separated from the bulk of the iron by Johnson's method, and the hydrochloric acid solution of this precipitate is then treated with sodium hydroxide and sodium peroxide as described by Noyes, Bray and Spear.[2] It is hoped that this treatment will quantitatively precipitate iron, zirconium, titanium, and cerium, leaving such elements as aluminum, uranium, vanadium, chromium, tungsten, molybdenum, and phosphorus in solution. Iron, manganese, and the greater part of the copper, nickel, and cobalt are next separated by precipitation with ammonium sulfide in the presence of tartrate as recommended by Thornton,[3] and zirconium, titanium, (and cerium) are finally precipitated by ammonia after destroying the tartaric acid. The ignited and weighed precipitate is then treated for titanium and the rare earths as described in the Bureau method.

(D) CONFIRMATORY EXPERIMENTS

Table II gives a summary of the data obtained in the analysis of the Bureau of Standards acid-open-hearth steel No. 20*a* to which definite amounts of standardized solutions were added.

TABLE II

No.	V Pres. G.	Cr Pres. G.	Cu Pres. G.	Ni Pres. G.	Al Added G.	Al Found G.	Ti Added G.	Ti Found G.	Zr Added G.	Zr Found G.
1	0.0005	0.0009	0.0034	0.0009	None	None	None	None	None	None
2	0.0005	0.0009	0.0034	0.0009	None	None	None	None	None	None
3	0.0005	0.0009	0.0034	0.0009	0.0100	0.0101	0.0100	0.0102[1]	0.0101	0.0097[3]
4	0.0005	0.0009	0.0034	0.0009	0.0100	0.0094	0.0100	0.0102[1]	0.0101	0.0097[3]
5	0.0005	0.0009	0.0034	0.0009	0 0500	0.0502	0.0476	0.0482[2]	0.0500	0.0493[3]
6	0.0005	0.0009	0.0004	0.0009	0.0500	0 0501	0.0476	0.0482[2]	0.0500	0.0492[3]

[1] Colorimetrically.

[2] Volumetrically after reduction in a Jones reductor and collection in ferric alum solution.

[3] The special treatment for vanadium (see Note 2) was not carried out. This furnishes an interesting light on the slightly higher values for titanium obtained both colorimetically and volumetrically and the correspondingly lower values for zirconium which resulted on account of the omission of this step.

V—SUMMARY

This paper presents a critical review of published and theoretical methods for the determination of zirconium in steels, and gives a method for the determination of silicon, aluminum, titanium, and zirconium in steels containing other probable or possible alloying elements such as tungsten, chromium, vanadium, phosphorus, molybdenum, copper, nickel, cobalt, uranium, and cerium.

The authors desire to express their thanks to Dr. W. F. Hillebrand for valuable suggestions and advice, and to Mr. J. R. Eckman for help in experimental work.

THE TITRATION OF AMMONIUM ACID FLUORIDE

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Received December 13, 1919

Some time ago acidity estimation on ammonium acid fluoride was added to the routine tests of the analytical laboratory. A fairly complete search of the literature failed to reveal any method for this determination, but it was learned that direct titration with standard sodium hydroxide in the presence of chipped ice, using methyl orange as an indicator, was more or less successful. That procedure was tried, but proved to be entirely unsatisfactory, owing to the indefiniteness of the end-point.

Ordinarily the titration of an acid salt of a strong mineral acid is easily accomplished. The case of ammonium acid fluoride is an exception, owing to the fact that none of the common indicators, namely, phenolphthalein, methyl orange, litmus, lacmoid, methyl red, and cochineal, act satisfactorily. Phenolphthalein is eliminated because of the influence of ammonium salts, and the other five indicators are useless because of erratic end-points in titrating hydrofluoric acid.

It was evidently necessary for the titration of this material that either ammonia or the fluorine be removed. The following method, based on precipitation of fluorine by calcium chloride and titration of the equivalent hydrochloric acid liberated, was consequently evolved.

PROCEDURE

Weigh 1.3 to 1.4 g. of material in a small weighing bottle (which is coated on the inside with paraffin to about three-fourths of its depth), and transfer to a 400-cc. beaker with cold water, taking care to keep the volume down to about 125 cc. The material dissolves rapidly, but solution is hastened by stirring, and the fluoride is immediately precipitated by adding a solution consisting of 5 to 6 g. of C. P. calcium chloride dissolved in about 75 cc. of water and neutralized (as is always necessary owing to the CaO present) with dilute hydrochloric or sulfuric acid using methyl orange as an indicator.

The mixture is stirred thoroughly for about a minute, and titrated with 0.5 *N* sodium hydroxide to the usual end-point, with the modification that the latter should be permanent for at least 2 min. More methyl orange is added if necessary to produce a distinct color.

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[1] *Loc. cit.*

[2] *Technology Quarterly*, **21** (1908), 35.

[3] *Am. J. Sci.*, **37** (1914), 173.

The white CaF_2 usually remains suspended in the liquid, but does not obscure the end-point, which is obtained readily after some experience. In this connection it might be helpful to use a blank at first, and for this purpose the first sample titrated answers very well if it is treated with about one cc. excess of the standard sodium hydroxide in order to keep the end-point permanent for an extended period.

REMARKS

The method is rapid and reasonably accurate and therefore provides a welcome release from long and tedious gravimetric procedures.

High-grade commercial ammonium acid fluoride contains between 90 and 95 per cent NH_4HF_2, and with the above method there is no difficulty in obtaining, after some practice, results accurate to about 0.5 per cent of the actual acid fluoride content.

The method is applicable to lower-grade material, that is, to a mixture in any proportion of the acid and normal fluoride.

As might be expected, the other indicators which behave like methyl orange toward hydrofluoric acid are also made applicable by this method. The usual C. P. grade of calcium chloride contains enough heavy metal impurities to precipitate cochineal indicator, but use of the latter is limited by that factor only. Methyl orange, lacmoid, and methyl red give quite similar results, but, in our experience, litmus tends toward somewhat high values.

SUMMARY

A rapid, reasonably accurate method for titrating ammonium acid fluoride is described, depending on the removal of hydrofluoric acid and titration of the equivalent hydrochloric acid liberated, thereby permitting the use of one of the common indicators.

THE DIAZOMETRIC DETERMINATION OF PHENOL, AND OF CERTAIN OF ITS HOMOLOGS

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Received October 27, 1919

In searching for a practical "field test" for determining the strength of cresylic acid solutions extensively used by the Bureau of Animal Industry in official disinfecting operations, a study has been made of the diazometric method applied to the lower monohydric phenols of the benzene series. The investigation appears to possess some practical value, and to be in a field not covered by existing literature.

The method depends upon the quantitative coupling of phenols with diazonium salts to form insoluble hydroxyazo compounds, as in the equation

$$C_6H_5OH + N : N(OH)Ar = HO.C_6H_4N : N.Ar + H_2O.$$

Schwalbe,[1] followed by Bucherer,[2] developed it into an accurate method for the determination of β-naphthol and some of its derivatives and formulated the general conditions and precautions necessary. These may be summarized as follows:

1—A sufficiently stable and reactive diazo solution.

2—A normally reacting phenol or mixture of known mean molecular weight.

3—An azo compound sufficiently insoluble so that the end-point may be unobscured and that secondary formation of disazo compounds may not vitiate the results.

4—The presence of an appropriate buffer to maintain hydrion concentration within such limits that coupling may be speedy and complete but that conversion of diazonium hydrate into the inactive isodiazo compound may not take place.

5—The absence of interfering substances such as amines or ammonia.

Schwalbe and Bucherer titrated with a solution of *p*-nitrobenzene diazonium chloride, which, being unstable, required standardization shortly before use. Since the diazotization of *p*-nitraniline is rapid and quantitative under properly controlled conditions it seemed that a serious drawback might be avoided if the solution of *p*-nitraniline itself was made the standard solution, diazotization being performed just before each titration. Therefore, approximately 14 g. of C. P. *p*-nitraniline were dissolved in a flask on the steam bath with about 400 cc. of water and 70 cc. of C. P. colorless[1] concentrated nitric acid, heated 2 hrs. and allowed to cool over night. The impurities separated and agglomerated by this treatment were filtered off and the filtrate was diluted to one liter, thus making an approximately 0.1 *N* solution. When a titration was to be performed a carefully measured volume (25 or 50 cc.) of a one per cent solution of C. P. sodium nitrite was placed in a dry flask and exactly the same volume of the *p*-nitraniline solution was run in with constant and thorough agitation. The mixture was allowed to stand 5 min. before use. Repetition of this process with different solutions employed for scores of titrations over a period of several months yielded invariably consistent results. Provided the mixing is properly performed with a sodium nitrite solution that is not too weak, the fresh diazo solution is clear and only slightly yellow, and therefore contains no appreciable quantity of the diazoamino compound.

The diazo solution (and consequently the original *p*-nitraniline solution) was standardized against β-naphthol as described by Schwalbe. Into a large beaker were brought 20 cc. of an exactly 0.1 *N* solution of β-naphthol[2] (14.4114 g. per liter), about 500 cc. water, acetic acid to neutralize, if necessary, and 15 g. of crystallized sodium acetate. The diazo solution was run in from a burette with constant stirring. Approach to the end-point was ascertained roughly by spot tests on filter paper or on a spot plate, and precisely by filtering 10 to 20 cc., dividing the filtrate between two specimen tubes and testing, respectively, with a drop of diazo solution and a drop of β-naphthol solution.[1] Upon close approach to the end-point, about 5 min. must be allowed before filtration to insure complete coupling, and the tests should be held under observation for the same length of time.

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[1] *Ber.*, **38** (1905), 3071.

[2] *Z. angew. Chem.*, **20** (1907), 877.

[1] Rendered colorless by blowing with air. Nitric acid was chosen on account of the presence of lead salts in the liquids titrated.

[2] The "recrystallized, medicinal" substance is reputed very pure. In fact recrystallization from dilute alcohol after filtration through blood charcoal did not raise its apparent purity. The material may be dissolved in aqueous caustic soda but since such a solution rapidly decomposes, dilute alcohol (400 cc. per liter) was a preferable solvent.

Schwalbe stated that the deterioration of a diazo solution, besides being dependent upon light and temperature, is hastened by excess of nitrous acid and is retarded by excess of strong mineral acid. Since the solution employed exceeded the ordinary in both these particulars a determination of the rate of deterioration was desirable. 400 cc. were therefore prepared as usual except that the sodium nitrite solution was made one-half stronger, namely, 1.5 per cent. The value of the solution against 20 cc. 0.1 N β-naphthol was determined firstly when fresh, and secondly after standing in the mixing flask covered with an inverted beaker for 5 hrs. in diffused daylight in front of a window at a temperature of 28° to 29° C. The average results were 40.2 cc. and 40.6 cc., respectively, a loss of 1 per cent in 5 hrs., which is insignificant under the conditions recommended for practice.

The monohydric phenols of the benzene series are far less amenable than β-naphthol to accurate determination by the diazometric method. Coupling is much slower in the absence of a marked excess of either component, which necessitates (1) working with as concentrated solutions as practicable, and (2) the selection of a buffer which will maintain the lowest possible concentration of hydrion without notable formation of isodiazo compounds.

Moreover the resulting azo compounds are more soluble, which, added to the necessarily longer time of exposure, renders the production of disazo compounds a more important source of error. Conditions most favorable for one phenol may be inappropriate for another, and inasmuch as the aim was to obtain a method applicable to mixtures it was necessary to reach a compromise. Meta- and *p*-cresols offered the most difficulties; phenol and *o*-cresol the least. After many experiments basic lead acetate as purchased in dry form "for sugar analysis" was chosen as the most appropriate buffer. It also possesses the important virtue of forming lead azo salts less soluble than the corresponding sodium salts, with consequent reduction of errors caused by the formation of disazo compounds. Its greatest drawback is an apparent tendency to precipitate certain phenols, or to induce complex combinations thereof, most marked in the case of *m*-cresol, so that low results may be avoided only by introducing it *pro rata* during the titration. For some reason the results are rendered more uniform and accurate by the simultaneous presence of sodium acetate.

In the procedure finally adopted 20 cc. of an approximately 0.1 N solution of the phenol[1] are pipetted into a 250 cc. beaker, diluted with 50 cc. of a 10 per cent solution of crystallized sodium acetate, and the liquid rendered neutral to litmus, if necessary, with acetic acid. Fifty cc. of basic lead acetate solution (30 g. in 100 cc.) are measured in a graduated cylinder, and approximately 10 cc. are added to the phenol solution. Then the freshly prepared diazo solution is run in from a burette with constant stirring, and as each 10 cc. mark on the burette is reached another 10 cc. portion of the basic lead acetate is added to the liquid under titration. When the end of the titration is near at hand, the liquid is left at rest 2 min., then again thoroughly stirred. A 7 cm. filter is folded, opened into a cone, and slipped down the inside of the beaker with the triple-thick side in contact with the glass, until well immersed. It will become wet through in a few seconds and will then remain in position when the finger is removed.[2] From the liquid filtering into the well thus formed a portion is removed by a medicine dropper and two cups in a porcelain spot plate are filled nearly full. To one cup is added one drop of diazo solution, to the other one drop of the original solution of the phenol under examination.[3] If no color develops in either cup in a few seconds, one drop of strong caustic soda (about 25 per cent) is added to each, and the plate held under observation for not longer than 10 seconds. If the end-point is at some distance on either side the distinction will be very sharp, but if near at hand a strong color may develop in both cups owing to incompleteness of the coupling. In that case one may wait a sufficient length of time and then repeat the filtration and test, or may note the result as a provisional end-point and continue the titration with liberal additions of the diazo solution until the end-point is clearly passed. The limits thus coarsely defined by the first titration are narrowed down by subsequent titrations to the desired degree of precision. In these it is necessary to observe that:

1—The time necessary to wait before filtering for a test depends on the degree of accuracy desired, and the nearness of the true end-point, 20 min. being the maximum.

2—After adding caustic soda to the tests, decision must be made in a few seconds, for the liquid in the cup containing an excess of diazo solution soon becomes brown from decomposition, and a red tint is likely to develop in both cups merely from the effect of the caustic soda upon traces of lead azo salts carried through the filter.[1]

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[1] In view of a suggestion that the above description may not be clear to those unversed in certain branches of chemistry it may be explained that the addition of *p*-nitrobenzene diazonium salts (*i. e.*, diazotized *p*-nitraniline) to a solution of β-naphthol in presence of sodium acetate (to depress hydrion concentration) produces, by "coupling" in accordance with the type equation already given, a highly insoluble red precipitate of the hydroxyazo compound, technically of considerable importance under the name "paranitraniline red." If, therefore, at any stage of the titration a portion of the liquid be filtered and the resulting colorless liquid divided into two parts and tested with diazo solution and β-naphthol solution, respectively, the stage of progress of the titration will be accurately indicated by the appearance, or non-appearance, of a red color in one, or neither, of the two tubes.

[1] Phenol and the cresols were redistilled and a portion of the middle third of the distillate was dissolved in water. The supply of the xylenols was so limited that portions were simply heated to fuming in small tubes immersed in a sand bath. The xylenols were dissolved by means of caustic soda.

[2] This convenient method for filtering small portions of liquid for test was demonstrated to the writer in 1914 by Mr. R. G. Mewborne.

[3] To insure clearness it may be noted that the rationale of the process is the same as explained in a previous footnote with reference to the standardization of the *p*-nitraniline solution. Differences in details are simply consequent upon the sluggishness with which a diazo solution reacts with phenols of the benzene series as compared with the reaction with β-naphthol. The tests for the end-point may be made in tubes if these are preferred to the spot plate.

3—Successive small additions of diazo solution are likely to cause too high results, hence tests on the under side are entirely reliable only when made after the addition of a single quantity of diazo solution.

In practice, after the first approximation, much time may be saved by executing the later titrations simultaneously.

The percentages of recovery obtained in the experiments were:

Phenol	99.75
o-Cresol	99.67
m-Cresol	100.84
p-Cresol	100.60
o-Xylenol (1:2:4)	100.54
p-Xylenol (1:4:2)	100.66

Other xylenols were not available. Far too high results were obtained on thymol, apparently from the formation of disazo compounds.

Equal parts of the solutions of phenol and the cresols used above were mixed and the mixture was titrated. The result was identical with the theoretical figure calculated from the titrations of the original solutions. The table will illustrate the general method of procedure.

Titration No.	Tested at Cc.	Time of Standing Min.	Results of Tests	
1	30.0	2	Strongly under, before NaOH added	
	33.0	2	Strongly under, before NaOH added	
	36.0	2	Colored and turbid filtrate	
	..	5	Doubtful	
	39.0	3	Strongly over, before NaOH added	
2	36.0	10	Strongly under, after NaOH added	
	37.5	10	Strongly over, before NaOH added	
3	36.8	10	Doubtful	
	..	20	Slightly, but distinctly under	
	37.2	20	Slightly, but distinctly under	
4	37.2	20	Faintly under	Mean result 37.3 cc.
	37.4	20	Over	

Inasmuch as Bader[2] described a gravimetric azo method for certain phenols, it appeared possible that after a titration the contents of the beaker might be acidified with dilute nitric acid, and the azo compound extracted with ether and weighed. Though preliminary experiments with some phenols were promising, the results with others, notably *m*-cresol, were so badly affected by secondary reactions that further work on developing a general method along this line was abandoned.

In conclusion it may be added that preliminary experiments upon the development of a field test for cresol solutions used as animal dips have been rather encouraging. The results are not affected by the soap present in such solutions, while the basic lead acetate employed appears to precipitate and render innocuous organic matter derived from the animals (hogs).

SUMMARY

A 0.1 *N* solution of *p*-nitraniline nitrate is satisfactorily permanent in the dark, and from it a reliable 0.05 *N* diazo solution may be prepared by properly mixing with an equal volume of sodium nitrite solution.

The diazometric determination of the lower monohydric phenols of the benzene series was found practicable with the use of basic lead acetate as a buffer under restricted conditions, and may be sufficiently accurate and convenient to be of value for certain technical purposes.[1]

A NEW METHOD FOR THE DETERMINATION OF ACETIC ACID IN ACETATES

By Oscar A. Pickett

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Received December 10, 1919

At the time of the development of the method to be described, it was desirable to have a fairly rapid and convenient method for the determination of acetic acid in sodium acetate and in residues containing small amounts of sodium acetate and free acetic acid. Several of the modifications of the phosphoric acid method, which had been considered most satisfactory, were tried,[2] but none were found satisfactory for control work under conditions then existing in our laboratory, for two main reasons: the time required to complete an analysis was too long, and it required too much experience and skill on the part of the analyst to secure the desired accuracy.

The old method consisted of a distillation of the sample with water and phosphoric acid, more water being added and the distillation repeated, until all the acetic acid was driven over. By none of the modifications of the old method was it possible to reduce the actual time of distillation to less than one and one-half hours. The main and essential difference between the present method and the old method is that the acetic acid set free by the phosphoric acid is carried over by a current of xylene vapor instead of water vapor. Detailed directions for carrying out analyses by the new method are stated below.

PROCEDURE

Weigh out a 2.5-g. sample of the material to be analyzed into a 500-cc. flat-bottomed flask. Add 30 to 40 cc. of distilled water to dissolve the sample, 20 cc. of 85 per cent phosphoric acid, free from all volatile acids, and 350 cc. of xylene. Connect the flask by means of a distilling bulb to a condenser (a 24-in., bulb-type condenser is most desirable) and distil from an electric hot plate. An open flame should not be used because of danger from fire. Collect the distillate in a 1000 cc. flask. Continue the distillation until only a thin film of xylene remains over the surface of the phosphoric acid solution. At this point all acetic acid will have been carried over, along with some hydrochloric acid, if chlorides are present in the material being analyzed. Also, any formic acid or higher homologs of acetic acid present will be distilled over along with the acetic acid. Do not carry the distillation further than the point indicated, as some phosphoric acid may at this point begin to be carried over with the last traces of the xylene. The distillate usually separates into two liquid layers. The upper layer consists of xylene, with some acetic acid dissolved in it, and the lower layer consists of a water solution of acetic acid. Titrate for total acidity in the distillate with 0.33 *N* carbonate-free sodium hydroxide, using phenolphthalein as an indicator, and taking care to neutralize all acid dissolved in the xylene layer. After correction of the burette readings for calibration and temperature variation,

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[1] Uncertainty arising from the latter source may be partly eliminated by making the test in three cups, adding to the middle one, as a blank, only the caustic soda.

[2] *Buletinul societătii de sciinte din Bucuresci*, **8** (1899), 51.

[1] In the introduction it was noted that one of the general conditions prerequisite to successful use of the method is "a normally reacting phenol or mixture of known mean molecular weight." Under the conditions prescribed it has been shown that normally reacting phenols include phenol, the three cresols and two of the xylenols, while thymol must be excluded. Tests on other phenols of the series, including other xylenols, must be left to those who have the substances available. Technically occurring materials containing phenols frequently contain them in admixture. For example, technical cresol may contain variable but often considerable amounts of both phenol and xylenol. Since the molecular weight of phenol is 94.08, of cresol 108.10, and of xylenol 122.12, it is obvious that the judgment of the analyst must be called upon to decide the applicability of the method to his needs, and the factor which should be employed for calculating results.

[2] *J. Soc. Chem. Ind.*, **23** (1904), 305, 530; THIS JOURNAL, **1** (1909), 250; **10** (1918), 550; Lunge, "Technical Methods of Chemical Analysis," *Trans.*, **3**, 307; Allen's "Commercial Organic Analysis," **1**, 507.

$$\frac{\text{Cc. of alkali} \times \text{normality factor} \times 6.0}{\text{Weight of sample}} =$$

A = Total acidity as acetic acid.

If chlorides were present, make a correction for the hydrochloric acid which was distilled over, as follows: Add potassium chromate indicator to the distillate after the above alkali titration, and titrate with 0.1 *N* silver nitrate. Then,

$$\frac{\text{Cc. silver nitrate} \times \text{normality factor} \times 6.0}{\text{Weight of sample}} =$$

B = Acetic acid equivalent of the hydrochloric acid present.

A — B = Organic acids as acetic acid.

Typical results by the new method are given in Table I. These were obtained by high school students trained in our laboratory and by graduate chemists. Large amounts of chlorides were present in the samples analyzed. These, however, did not in any way prevent accurate results from being obtained for the acetic acid values.

TABLE I—DETERMINATIONS OF ACETIC ACID VALUES BY NEW METHOD

No.	DESCRIPTION	Total Acidity as CH_3COOH Per cent	HCl as CH_3COOH Per cent	Actual CH_3COOH Per cent	Difference between Checks
3,610	Residue	61.14	56.23	4.91	
		59.30	54.39	4.91	0.00
3,616	Residue	59.79	54.17	5.62	
		61.61	56.02	5.59	0.03
3,637	Residue	61.44	58.85	4.59	
		48.53	43.90	4.63	0.04
3,946	Sodium Acetate	69.28	19.60	49.68	
		68.49	18.81	49.68	0.00
3,974	Residue	61.26	52.74	8.52	
		61.50	53.00	8.50	0.02
4,394	Sodium Acetate	75.80	14.55	61.25	
		76.29	14.84	61.45	0.20
4,491	Sodium Acetate	56.68	21.01	35.67	
		57.47	21.85	35.62	0.05
4,501	Sodium Acetate	59.43	21.73	37.70	
		60.24	22.72	37.52	0.18
4,541	Sodium Acetate	67.58	18.63	48.95	
		68.57	19.50	49.07	0.12
4,851	Sodium Acetate	68.85	19.93	48.92	
		68.82	19.91	48.91	0.01
9,944	Calcium Acetate	55.78	14.02	41.76	
		55.88	14.11	41.77	0.01
10,066	Calcium Acetate	57.15	12.70	44.45	
		56.82	12.58	44.24	0.21
10,232	Calcium Acetate	56.64	14.26	42.38	
		55.98	13.51	42.47	0.09
10,271	Calcium Acetate	45.38	5.61	39.77	
		43.22	3.60	39.62	0.15

In order to check the xylene distillation method against pure materials of known strength, tests were made upon pure acetic acid and upon chemically pure sodium acetate. A dilute solution of acetic acid was analyzed by direct titration against standard 0.33 *N* sodium hydroxide solution and also by the xylene method as described above. A sample of pure sodium acetate was also analyzed by this method. This material was tested for purity and strength by determining the sodium content by smoking off with sulfuric acid, according to the usual method of determining metals in organic salts. From the amount of sodium sulfate formed, the percentage of $CH_3COONa.$-$3H_2O$ was calculated. The results are shown in Table II.

TABLE II—CHECK ANALYSES ON PURE MATERIALS (PER CENT)

	ACETIC ACID		SODIUM ACETATE	
SAMPLE No.	CH_3COOH by Xylene Distillation and Titration	CH_3COOH by Direct Titration	$CH_3COONa.3H_2O$ by Xylene Distillation and Titration	CH_3-$COONa.3H_2O$ by Conversion to Na_2SO_4
1	19.62	19.58	100.00	100.00
2	19.50	19.58	100.03	100.07
3	19.63	19.59	99.92	99.80
4	19.65	19.68	....	99.80
AVERAGE	19.60	19.61	99.98	99.92

The new method has been used continuously in our laboratory for more than a year, and has been found to be very satisfactory, both as to time required for an analysis and as to the ease with which considerable accuracy is attained. It has been adopted in the analysis of sodium acetate, commercial calcium acetate, and sodium acetate residues carrying from 0 to 10 per cent of acetic acid. With all of these materials the method gives accurate results. It has also been used successfully for the determination of propionic and butyric acids in their salts. As to the time required to make a complete analysis, it has been found that 45 min. are usually sufficient.

SUMMARY

A method has been developed whereby acetic acid in its salts can be determined.

The former difficulty of obtaining accurate results has been eliminated by using xylene, instead of water, as a carrier for the acetic acid in the distillation of the acetate with phosphoric acid.

The usual time required for an analysis has been greatly reduced.

The method has been used for factory control over a considerable period, and can be recommended for use in technical laboratories.

INDICATORS USED FOR DETERMINING FREE ACID IN PICKLING SOLUTIONS

By C. L. Boyle

THE STUDEBAKER CORPORATION, DETROIT, MICHIGAN

Received December 10, 1919

The usual method for determining the amount of free acid in pickling solutions consists in titrating 10 cc. quantities of the pickling solution with standard alkali, using either phenolphthalein or methyl orange as the indicator. The presence of a large amount of ferrous sulfate renders the end-point with either methyl orange or phenolphthalein very hard to see. Of the two, methyl orange is to be preferred. Either sodium or potassium thiocyanate, however, can be used, enabling the analyst to recognize the end-point more easily.

The use of either sodium or potassium thiocyanate is based on the facts that iron is always present in a pickling solution, and that ferric thiocyanate is deep red in acid solution, but loses this color the minute the solution becomes alkaline.

The following procedure is recommended for use of this indicator:

To a 10-cc. sample of the pickle liquor at a temperature of about 70° F. add several drops of a concentrated solution of either sodium or potassium thiocyanate. Without diluting, titrate the solution with standard alkali until the red color of the ferric thiocyanate entirely fades, leaving the solution a greenish yellow.

In connection with this titration, it may be pointed out that the coloration is more intense when the solution is used undiluted and that if the color does not develop at first, the addition of the alkali soon brings it out.

The selection of the standard alkali depends upon whether the results of the titration are to be expressed as percentage acidity by weight, percentage acidity by volume, or pounds of anhydrous sulfuric acid per cubic foot of pickling solution. A standard normal solution of sodium hydroxide will be found convenient for expressing the percentage by volume or by weight. In this case each cc. of normal alkali represents approximately one per cent of free acid by volume. A 0.816 *N* solution of sodium hydroxide will be found convenient for expressing the results of the titration in pounds of sulfuric acid per cubic foot. Here the number of cc. of standard alkali used to titrate 10 cc. of pickling solution multiplied by 4 will represent the number of pounds of anhydrous sulfuric acid present in each cubic foot of the pickling solution.

In making the standard alkali solution it must be borne in mind that this indicator, though of constant accuracy, gives an end-point slightly on the alkaline side and it is therefore necessary to use this indicator when making up the standard solution. The addition of some iron salt like ferrous sulfate to the acid solution which is used to titrate against the alkali solution in standardizing the latter gives the necessary iron content to the solution and is without influence on the titration. By this means a condition parallel to the actual titration of the pickling solution is obtained.

SOY-BEAN OIL

By Wilson H. Low

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Received December 18, 1919

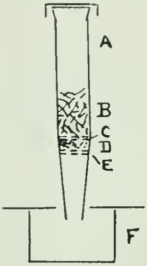
A sample of filtered soy-bean oil was examined for total fatty acids, unsaponifiable matter, and glycerol, by calculation.

Fifty grams of the oil were saponified by boiling for 1.5 hrs. under a reflux condenser with about 600 cc. of approximately 0.5 *N* alcoholic potash solution.

UNSAPONIFIABLE MATTER—The solution was transferred to a separatory funnel, diluted with water to a volume of 2400 cc., and extracted with 750 cc. of ethyl ether, followed by five more extractions of 250 cc. each. The ether residue (unfortunately not examined for free fatty acids) amounted to 1.16 per cent, recorded as unsaponifiable matter. This is probably higher than would be found had a correction been made for free fatty acids with the residue.

FATTY ACIDS—The solution, presumably free from unsaponifiable matter, was evaporated to dryness in a large porcelain dish, treated with water, again evaporated to pastiness, and finally dissolved in water, and the fatty acids set free with dilute hydrochloric acid. The mixture was transferred to a separatory funnel and washed free from mineral acid, as indicated by methyl orange. The washings were combined and subsequently extracted with ether.

The melted fatty acids were allowed to stand warm in the separatory funnel and from time to time the water which had collected upon rotating the funnel was drawn off, until finally very little was in evidence. The clear melted fatty acids were then drawn into a filtering tube illustrated by the accompanying figure.



A = Filtering tube, about one inch inside diameter, but any size is possible

B = Shredded or rasped filter paper, well dried

C = Perforated porcelain disc

D = Asbestos mat for filter

E = Another perforated porcelain disc

F = Weighed crystallizing dish, protected from dust by a piece of cardboard

Shredded, or, better, rasped filter paper, if well dried, will absorb considerable moisture and be without action on the fatty acids. By maintaining the arrangement at a low temperature, yet sufficiently high to keep the contents well melted, the fatty acids percolated through into the dish. Filtration was allowed to go on over night.

The aqueous washings were extracted with more ether, the separatory funnel washed out with ether, and all the extracts combined and the fatty acids recovered.

Fatty Acids	Grams	Per cent
Recovered directly	39.7080	....
Recovered in ether extracts, etc.	7.7752	....
Total (Free from unsaponifiable matter)	47.4832	94.966
Unsaponifiable matter	...	1.160
Total (Ordinary fatty acids)	...	96.126

In weighing the fatty acids a constant slight gain was noted. This was probably due to oxidation, as the dish and fatty acids had remained in the balance case a long time before weighing. If oxidation was the cause, it must also have been going on during the time of filtering, and our result would be slightly high.

GLYCEROL—Ten grams of the original oil (refined and practically free from free fatty acids) were saponified with standard alcoholic potash solution. The alkali consumed was equivalent to 33.80 cc. of *N* solution, or ($33.8 \times 0.02168 = 0.732784$ g.) 7.33 per cent of glycerol anhydride or 10.37 per cent of glycerol.

It may be said in passing that this method of determining glycerol, if properly and carefully followed, is as accurate as any other known method. If there are any free fatty acids present in the oil they must be allowed for, using the true combining weight of the pure (free from unsaponifiable matter) fatty acids, which is given below, as the result both of calculation and experiment.

Impure fatty anhydrides + unsaponifiable matter (100.00 — 7.33) = 92.67 per cent
Calculated combining wt. of impure fatty anhydrides = 274.17
Calculated combining wt. of impure fatty acids (274.17 + 9.01) = 283.18
Pure fatty anhydrides (92.67 — 1.16) = 91.51 per cent
Calculated combining wt. of pure fatty anhydrides = 270.73
Calculated mean combining wt. of pure fatty acids (270.73 + 9.01) = 279.74

Five grams of the recovered pure fatty acids (39.708 g.) were saponified by boiling with excess of alcoholic potash and their combining weight determined. The actually determined mean combining weight found was 279.3, agreeing closely with the calculated value.

IODINE ABSORPTION—*Wijs Method*—The lower values in the case of the fatty acids shown below are due to the fact that they did not contain the unsaponifiable matter, which itself would have absorbed iodine, and also probably to some oxidation of the acid.

Iodine number of original oil	138.45 and 137.39
Iodine number of the pure fatty acids	132.83

SUMMARY

Total pure fatty acids in sample soy-bean oil	94.966	per cent
Unsaponifiable matter (+ possibly some free fatty acids)	1.16	per cent
TOTAL	96.126	per cent
Glycerol	10.37	per cent
Combining weight of ordinary fatty acids	283.18	per cent
Combining weight of pure fatty acids	279.30	per cent

THE PROXIMATE COMPOSITIONS OF KOREAN HEMP AND RAMIE

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Received December 31, 1919

INTRODUCTION

This paper is the first of a series of reports on Korean bast fibers from the standpoint of textile chemical research. Hemp and ramie have long been the most important raw textile materials in Korea. The former, grown throughout the country, is much larger in output than the latter and its bast fiber is obtained by an artificial retting process combined with scutching, and a spinning operation performable only by skilled hand labor. The latter, which is the chief textile fiber of China and known as China grass, is limited in locality and has a smaller output, but its quality is excellent and textiles made from it are highly valued as summer cloth in Korea. The treatment of the ramie fiber is a kind of "dew retting," a treatment commonly applied to all bast fibers, followed by the same scutching and spinning operations as are used upon the hemp fiber.

In the course of experiments on bleaching the Korean hemp and ramie weaves which were made at the Central Experiment Station, General Government of Korea, by the present author, several difficulties were found. For example, the whiteness was not entirely satisfactory, the loss of weight after bleaching was considerable, and the strength of the weaves was much weakened by the treatment. In order to overcome these troubles, it is necessary to have ample knowledge of the chemical composition of the fibers and their behavior toward various reagents. Another important reason which led to the present research is the fact that the chemistry of the pectocelluloses, among which hemp and ramie are classified, is still obscure and offers many problems for investigation.

The first step, therefore, is the consideration of the proximate composition of these fibers. Generally speaking, we have very little knowledge of the chemical constitution or even the proximate composition of the "compound" celluloses, not only pectocellulose, but also ligno- and adipocellulose. Methods of procedure for satisfactory analysis of compound celluloses are practically absent from the literature. Müller[1] gave analytical results on hemp and ramie. He determined hygroscopic moisture, ash, water extract, fat and wax, and cellulose, estimated the residue by difference, and reported it as "incrusting and intercellular substances and pectic constituents." The present author[2] also reported analytical results for the Korean products, following Müller's scheme. Cross and Bevan[3] consider the question of "incrusting" morphological rather than chemical. As a starting point for further investigation it is very desirable to consider more accurate and complete proximate analytical methods. W. H. Dore[4] of this Station recently proposed a scheme for the proximate analysis of wood and applied it to the proximate analysis of certain California woods. It seemed possible that this proposed scheme of analysis might be quite applicable to the pectocellulose which was the subject of the present work.

As far as our present knowledge extends, it appears that the structural substances common to hemp and ramie consist chiefly of pectocellulose, together with lignin and substances extractable by organic solvents. According to Cross and Bevan,[5] pectocellulose is a substance which is decomposed by boiling with dilute alkali into insoluble cellulose and soluble non-cellulose derivatives (pectin, pectic acid, and metapectic acid). The material extracted by organic solvents consists chiefly of a fatty and waxy substance together with other substances of less frequent occurrence. The presence of lignin in both Korean hemp and ramie was noted by the author[6] in the previous paper. The proximate compositions of the fiber are included in this paper, together with a discussion of the methods of analysis and the results obtained.

EXPERIMENTAL

The samples which were used in this work were representative samples of Korean hemp and ramie of superior quality.

(1) Hemp (*Cannabis sativa*), retted and scutched. A single fiber has an average length of 1.2 to 1.3 meters and a breadth of 0.6 to 0.7 mm. It has a pale brown color.

(2) Ramie (*Bocheria nivca*), retted and scutched. A single fiber has an average length of 0.7 to 1.1 meters

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[1] Mathews, "Textile Fibers," **1904**, 191, 197.

[2] *J. Chem. Ind. Japan*, **21** (1918), 314; *Chem. Abs.*, **12** (1918), 2127 *J. Chem. Ind. Japan*, **21** (1918), 1043; *Chem. Abs.*, **13** (1919), 794.

[3] "Cellulose," 2nd Ed., p 214.

[4] THIS JOURNAL, **11** (1919), 556.

[5] "Cellulose," 2nd Ed., p 217.

[6] *Loc. cit.*

and a breadth of 0.2 to 0.6 mm. The color is pale yellow.

Both samples were prepared for analysis by cutting with sharp scissors into small pieces of an average length of one centimeter. Mason fruit jars were found to be convenient for keeping the moisture content constant throughout the experiments.

METHODS OF ANALYSIS—The analysis included the determination of loss on drying, extractives soluble in benzene, extractives soluble in alcohol, substances soluble in water, substances soluble in one per cent sodium hydroxide, cellulose, and lignin. The following methods of procedure were modified from those originally proposed by Dore for the analysis of wood.

Loss on Drying—Two-gram samples are put in a weighing tube, dried in a constant temperature electric oven at 100° C. for 16 hrs. (over night), and weighed.

Benzene Extract—The fibers, dried as above, are placed in an alundum thimble and extracted with 100 cc. of the solvent for 6 hrs. in a Soxhlet apparatus on a hot plate. After the solvent is evaporated the residual extract is dried for one hour at 100° C. and weighed.

Alcohol Extract—The extracted fibers are next subjected to extraction with 95 per cent alcohol, using exactly the same process as in the benzene extraction.

Water Extract—After extraction with benzene and alcohol, the above sample is dried at 70° to 80° C. to expel the adhering solvent, then digested with 100 cc. of distilled water in a 250-cc. Erlenmeyer flask fitted with a reflux condenser. After heating on a hot plate for 3 hrs., the sample is filtered, washed with hot water, dried for 16 hrs. at 100° C., and weighed. For filtration a Gooch crucible, with a mercerized cotton disc fitted in the bottom as proposed by Dore, is used. The weighing of the crucible, both before and after the filtration, is carried out in a glass-stoppered weighing bottle. The water-soluble material is calculated by adding loss on drying, benzene and alcohol extracts, and residue after water extraction, and subtracting this sum from the total weight taken.

Soluble in One Per Cent Sodium Hydroxide Solution—The dried residue after water extraction is transferred to a 250 cc. Erlenmeyer flask, 100 cc. of one per cent sodium hydroxide solution are added, and a reflux condenser fitted to the flask. It is then heated on the hot plate for one hour, filtered off on the same Gooch crucible, washed well with hot water, dilute acetic acid, and finally with hot water again, dried in the weighing bottle for 16 hrs. at 100° C., and weighed. The loss in weight of crucible and contents represents substances soluble in one per cent sodium hydroxide solution.

Cellulose—The dried residue from the alkali treatment is washed with water and the excess of water drawn off by suction. The crucible is placed on a filtering flask attached to a suction pump, and covered with a tightly fitting glass cap which is connected to a chlorine generator. A moderately rapid stream of washed chlorine gas is passed through the crucible for 20 min. with the help of suction, the passage of the gas being judged by the rate of passage of bubbles through a wash bottle containing water and attached to the chlorine generator. The crucible is removed and placed on another suction flask, and dilute sulfurous acid is immediately poured on the material, after which it is washed with water. The crucible and its contents are then placed in a 50-cc. beaker, sufficient 3 per cent sodium sulfite solution added, and the whole heated on the steam bath for three-quarters of an hour. The crucible is removed from the solution and placed on the suction flask, and the sulfite solution, together with the material which has floated into the beaker during the operation, is poured into the crucible, after which the contents are well washed with water. The chlorination and sulfite treatments are repeated 3 times, the periods of chlorination being 15, 15, and 10 min. After the last treatment with sodium sulfite solution, the material is thoroughly washed with hot water, placed in the glass-stoppered weighing bottle, dried at 100° C. for 16 hrs., and weighed.

Lignin—Another 2-g. sample is dried and extracted with benzene and alcohol in the manner described above, and, after the adhering solvent has been expelled by heating to 70° to 80° C., the fibers are transferred to a large Erlenmeyer flask and treated with 20 g. of 72 per cent sulfuric acid. The flask is rotated and shaken to moisten the material with acid, and allowed to stand at room temperature with occasional attention to see that all the material comes in contact with the acid. At the end of 3 hrs., 500 cc. of distilled water are added and the mixture is heated for 2 hrs. on the hot plate under a reflux condenser. The residue is filtered by suction on a tared Gooch crucible similar to that used in other determinations, washed well with hot water, dried in a weighing bottle for 16 hrs. at 100° C., and weighed.

ANALYTICAL DATA—The following results were obtained for Korean hemp and ramie:

TABLE I—PROXIMATE COMPOSITIONS OF KOREAN HEMP AND RAMIE
(Results in Percentages)

SAMPLE	HEMP	RAMIE
Loss on drying	8.83	10.50
Benzene extract	1.92	0.86
Alcohol extract	1.20	0.75
Water-soluble	4.50	3.79
Soluble in one per cent sodium bydroxide	18.53	17.27
Cellulose	62.42	65.88
Lignin	3.32	0.66
TOTAL	100.72	99.71

DISCUSSION

A critical discussion of the methods of analysis proposed by Dore[1] is presented in his paper. A brief discussion of the methods of analysis and results obtained is included here in order to consider the application of Dore's scheme to the analysis of bast fibers, and to study for the purpose of future work the proximate composition of the fibers from the standpoint of textile chemistry.

LOSS ON DRYING—The methods of drying cellulose material have been studied by a number of investigators. They should be considered, not only in regard to the two essential factors (temperature and duration of drying), but also from the standpoint of convenience as well as accuracy. Drying at 105° to 107° C. to remove all hygroscopic moisture was accepted by Schwalbe, Renker, and König and Hühn, and this method has been considered the standard method of drying. As to the duration of drying, Schorger[1] affirmed that, in the case of wood sawdust, the moisture content could be determined with sufficient accuracy by drying for 7 hrs. at 105° to 107° C. There is, however, no definite line of demarcation between hygroscopic moisture and water expelled due to the dehydration of cellulose itself. The term "absolutely dry" is therefore more or less conventional. The experiments by Schorger[2] on the effects of prolonged heating upon the weight of wood are to be taken as one of the proofs of the above statement. The method of drying practiced here and also by Dore may not be regarded as an accurate moisture determination, but as an arbitrary treatment. It is, nevertheless, to be regarded as the most logical, from the standpoint of convenience, for the proximate analysis of cellulose materials. Since the dryings at separate stages in the analysis are made in the same manner as in the determination of loss on drying, the results are strictly comparable. In view of the above considerations the results are expressed as "loss on drying" and not as "hygroscopic moisture."

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[1] *Loc. cit.*

Experiments were made on the time effect in determining loss on drying. Two grams of the fibers were put in a weighing tube, dried for 16 hrs. in an electric oven at 100° C., and weighed. They were then dried again for 16 hrs., and weighed. There was practically no difference between the first and second dryings.

	LOSS ON DRYING (PER CENT)	
SAMPLE	16 Hrs.	32 Hrs.
Hemp	8.81	8.86
Ramie	10.50	10.58

BENZENE AND ALCOHOL EXTRACTS—The amounts of extractives removed from hemp fiber by these solvents are considerable. The benzene extracts in both hemp and ramie are composed of brown waxy substances which redissolve readily in benzene. The alcohol extracts of the fibers give a light green solution, probably due to chlorophyl. They are obtained as brownish green pasty residues, part of which is insoluble in alcohol even in the boiling state. The substances soluble in these solvents, termed "oil-wax complex" by Cross and Bevan, are the constituents of the cuticular tissues of the fibers. The oil-wax complex in the bast fibers bears an important relation to the bleaching process for these materials, since one of the chief difficulties experienced in hemp and ramie bleaching consists in breaking down these impurities without injuring the bast fiber proper.[3] The analytical results show that hemp contains more of these impurities than ramie, and this fact suggests, as is actually the case, that the former is more difficult to bleach than the latter.

SOLUBLE IN WATER AND DILUTE ALKALI—Pectocellulose contains much material which is easily rendered soluble by hydrolyzing agents, especially by alkali. The determinations of material soluble in water and alkali under the prescribed conditions not only give the proximate compositions of the fibers, but also suggest their chemical behavior when these textile fabrics are subjected to treatment such as the scouring operation in the bleaching process. The determinations of "soluble in alkali" have hitherto been made in an open beaker, keeping the concentration of alkali constant. The use of the Erlenmeyer flask with a reflux condenser, as given in the present method of procedure, may be regarded as more logical as well as more convenient. In both hemp and ramie the substances soluble in alkali are considerable, and the main part is considered to be pectin substance. This is the characteristic constituent of the so-called "non-cellulose" of the pectocellulose, and is easily rendered soluble by the action of alkali. Our knowledge of the chemistry of pectin substance is mostly due to the original researches of Fremy and Chondnew, and there is need of much further investigation.

CELLULOSE—Various methods have been proposed for the determination of cellulose. Renker[1] compared these methods for various cellulose materials and concluded that of all the methods investigated, none was so satisfactory as Cross and Bevan's method of chlorination. For the chlorination, the method proposed by Sieber and Walter,[2] which has also been used by Johnsen and Hovey,[3] was suggested by Dore as most convenient. This method was used throughout the present work and its reliability confirmed. By the treatments with water and alkali preceding the chlorination, the greater part of the substances less resistant toward hydrolyzing agents is removed. The residue therefore probably consists of the most resistant cellulose, termed "ortho-cellulose" by König and Rump and "normal cellulose" by Cross and Bevan, together with a small quantity of lignified tissues. The loss in weight by chlorination after the alkali treatment is very small, as is shown in Table II.

TABLE II—LOSS IN WEIGHT BY CHLORINATION
(Percentage on Air-Dry Basis)

	HEMP		RAMIE	
SAMPLE	(1)	(2)	(1)	(2)
Residue after alkali treatment	65.11	64.93	67.48	67.81
Residue after chlorination (cellulose)	62.42	62.43	65.70	66.06
Loss in chlorination	2.69	2.50	1.78	1.75

In the course of the chlorination the sulfite solution becomes very brown. The main substance broken up by this treatment may therefore be regarded as lignified tissue. After chlorination the residues are pure white and readily and completely soluble in 72 per cent sulfuric acid, and their amounts are accordingly tabulated as the cellulose content of the fibers. That the alkali treatment before chlorination has an important effect on the yield of cellulose is shown by Table III.

TABLE III—EFFECT OF ALKALI TREATMENT ON THE YIELD OF CELLULOSE
(Percentages on Air-Dry Basis)

	CELLULOSE	
PRELIMINARY TREATMENT	HEMP	RAMIE
Benzene and alcohol extraction, alkali treatment omitted	71.49	76.69
After benzene and alcohol extraction, digested for 30 min. with one per cent NaOH	65.99	68.35
After benzene and alcohol extraction digested for one hr. with one per cent NaOH	62.42	65.88

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[1] THIS JOURNAL, **9** (1917), 561.

[2] *Loc. cit.*

[3] Cross and Bevan, "Cellulose," p. 80.

[1] Cross and Bevan, "Researches on Cellulose," **3**, 30.

[2] *Chem. Abs.*, **8** (1914), 1202.

[3] *Paper*, **21** (1918), 40.

The cellulose residues obtained by various alkali treatments differ apparently in their physical nature, and further chemical investigation is necessary. Such researches will be made shortly by the author.

LIGNIN—König[1] treated the extracted lignified materials with 72 per cent sulfuric acid according to the method of Ost and Wilkening,[2] and regarded the noncellulose residue as lignin. This method was recently applied by Dore for the determination of lignin in wood. The data for lignin in hemp and ramie given in this paper were obtained by König's method.

The lignin, which is believed by investigators to exist in combination with cellulose as lignocellulose, may not be a constituent of the bast fibers belonging to the pectocellulose proper. The cuticular tissue of the fibers in the stem, which is much lignified, occurs in intimate contact with the bast fiber and part of it remains after the scutching operation. It appears to the author that the determination of lignin in hemp and ramie serves as one of the indications of the completeness of the whole retting process.

The lignin is partly attacked by alkali digestion, and experiments were made on the effects of such digestion upon the yield of lignin. Two grams of the fibers were dried, extracted with benzene, alcohol, water, and one per cent sodium hydroxide as in the cellulose determination, and the lignin determination was made upon the dried residue as before. The results are given in Table IV.

TABLE IV—EFFECT OF ALKALI DIGESTION ON THE YIELD OF LIGNIN

	HEMP	RAMIE
Loss on drying	8.83	10.50
Benzene extract	1.92	0.86
Alcohol extract	1.20	0.75
Water-soluble	4.50	3.79
Soluble in 1 per cent sodium hydroxide	18.53	17.27
Cellulose	62.42	65.88
Lignin	1.99	0.18
TOTAL	99.39	99.23

SUMMARY

1—The proximate compositions of Korean hemp and ramie are given, as determined by modifications of the analytical method proposed by Dore.

2—The analytical results are discussed from the textile chemistry standpoint for the benefit of future investigations.

3—The presence of lignin in both hemp and ramie is confirmed quantitatively.

My sincere thanks are given to Mr. W. H. Dore for his kind suggestions and encouragement.

SHORT COMMERCIAL ANALYTICAL METHODS FOR THE DETERMINATION OF PURITY OF IMPORTANT CHEMICALS USED IN PYROTECHNICS

By Henry B. Faber and William B. Stoddard

NEW YORK, N. Y.

Received January 29, 1920

I—DETERMINATION OF SMALL AMOUNTS OF SODIUM IN THE PRESENCE OF LARGE AMOUNTS OF POTASSIUM

In potassium nitrate to be used in the manufacture of military pyrotechnics, the presence of salts of sodium is to be avoided for two reasons:

1—On account of the flame color imparted by small amounts of sodium compounds.

2—On account of the hygroscopicity of sodium nitrate, which might cause the finished articles to absorb moisture to such an extent as to interfere with their proper functioning.

The problem, therefore, became one of determining sodium nitrate in quantities as low as 0.01 per cent in potassium nitrate. Reference to the literature indicated that the method of Walter Craven Ball[1] was the only one available. This method is based upon the fact that when a solution of potassium nitrate, bismuth nitrate, and cesium nitrate, acidified with dilute nitric acid, is added to solutions of sodium nitrate, even in the presence of large quantities of potassium salts, the sodium is quantitatively precipitated as cesium sodium bismuth nitrite, having the formula $5\ Bi(NO_2)_3.9CsNO_2.6NaNO_2$. The precipitate is obtained in the form of large yellow crystals which are very easy to handle.

It was found convenient to modify the method used by Ball, who made the precipitation in a separatory funnel, the upper part of which was kept filled with coal gas. After the precipitate had entirely separated, it was removed by poking the crystals down through the stopper of the funnel. The present writer has found that a series of 30 cc. Erlenmeyer flasks can be used for making a number of determinations at the same time. One gram of each sample of potassium nitrate to be analyzed is dissolved in 5 cc. or less of water and placed in a flask. One cc. of 2 *N* nitric acid is then added and, by means of a pipette, 10 cc. of the reagent. The flasks are shaken and connected, and coal gas is passed through the series until the air has been replaced. The rubber tube at one end of the series is then closed by a glass plug, and the other end by a Bunsen valve, which is used in order to permit the escape of nitrous fumes which are developed in small amount. The cesium sodium bismuth nitrite begins to separate within a few minutes and collects on the bottom of the flasks as a yellow crystalline precipitate. The flasks should now be allowed to stand in a cool place for 48 hrs., during which time no scum should appear on the surface. The stopper is removed, and the flask rotated to loosen the precipitate from the glass, tilted to an angle insufficient for the liquid to run out, and the neck placed against an asbestos pad in a Gooch crucible.[2] The crucible, with the flask, is rapidly righted. The flask is now in an inverted position, the neck resting on the asbestos pad. In this position the flask and crucible are rotated with a slight vertical motion to wash all the precipitate from the bottom of the flask. The flask is then slowly raised, permitting the solution to enter the crucible, and the neck carefully withdrawn with a slight rotary motion to remove any adhering particles of the precipitate or asbestos.

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[1] *Chem.-Ztg.*, **36** (1912), 1101.

[2] *Ibid.*, **34** (1910), 461.

[1] *J. Chem. Soc.*, **95** (1909), 2126; **97** (1910), 1408. Full details as to the preparation of the reagent, and the technique and accuracy of the method are given in the second paper.

[2] This pad, which should fill one-third of the crucible, is prepared in the usual manner and finally washed with 10 cc. of 50 per cent acetone followed by 15 cc. of pure acetone in three portions, each portion being removed separately by suction. The crucible is then dried in an air bath at 100° for 30 min. and weighed.

The thickness of the asbestos pad is sufficient to prevent any of the solution from going through it until the crucible has been placed in a suction funnel. Suction is applied rapidly until three-fourths of the solution are passed through the crucible, when it is released. A small amount of the filtered solution is returned to the flask and a "policeman" used to remove any part of the precipitate that may have adhered to the glass. The liquid is then transferred to the crucible and suction again applied. The solution is rapidly filtered and the sides of the crucible and the precipitate are washed with 5 cc. of a 50 per cent acetone solution in a very fine stream. Suction is applied until the solution is passed through, and 15 cc. of pure acetone are added in 3 portions, each portion being passed through the filter by suction and the suction stopped before the next portion is added. The filtering operation is to be as rapid as possible, and a very small filter flask to be used, the object being to minimize exposure of the precipitate to the air in the presence of the reagent. Should a small amount of scum appear during the second filtration it may be disregarded, as it has no effect on the estimation. The filtrates should be perfectly clear before the acetone is used. The crucible is then dried in an air bath at 100° for 30 min., weighed or titrated as later indicated. The weight of the precipitate multiplied by 0.03676 will give the weight of the sodium calculated as metal.

VOLUMETRIC DETERMINATION

As the precipitate is a complex nitrite, it may be titrated by a standard solution of potassium permanganate, according to the following procedure:

After drying, the precipitate with the asbestos pad is transferred from the crucible to a beaker, 150 cc. of water added, followed by a known volume of a standard solution of approximately 0.1 *N* potassium permanganate in excess of the amount required for the oxidation. Forty cc. of sulfuric acid (1 : 1) are added and the solution heated to 70° C. The excess of potassium permanganate is titrated by means of a standard solution of approximately 0.1 *N* sodium oxalate. The available oxygen of the permanganate consumed under the acid conditions, multiplied by 7.820, will equal the weight of the cesium sodium bismuth nitrite. Since 30 atoms of oxygen are required for each molecule of the precipitate in order to convert the nitrites to nitrates, extended tests have established the availability of this volumetric method.

The cesium may be recovered from the filtrates by the addition of silver nitrate in slight excess, which precipitates a very insoluble cesium silver bismuth nitrite. This on heating and subsequent extraction with water yields a pure cesium salt.

From the factor given (0.03676), it will be seen that 1 mg. of sodium will produce over 27 mg. of precipitate and consequently the amounts of various materials to be used for analysis must be gauged according to their sodium content. From 3 to 8 mg. of sodium will be found to be a very convenient amount to be used in the application of this method.

II—DETERMINATION OF ALUMINUM IN ALUMINUM FLAKE OR DUST

As the use of finely divided metallic aluminum is essential in modern military pyrotechnic practice where the production of intense illuminations is desired, it is evident that a rapid and easy method for the determination of the metallic aluminum content of such material is of great value. As the presence of the usual small amounts of foreign materials, such as silicon and iron, does not interfere seriously with the result, the following methods may be more correctly designated as the determination of the total reducing power of the material rather than that of its metallic aluminum content.

The literature contains reference to two methods. One of these depends upon the volume of hydrogen which a sample of the metallic aluminum will liberate when treated with acid. In the case of flake aluminum this method is difficult to apply, owing to the fact that the material is so light that most of it floats. Another method depends upon the reduction of ferric sulfate to ferrous sulfate. The results from this method, however, were not uniform and very unsatisfactory, due no doubt to the formation of hydrogen during the reaction.

Attempts were made to use other oxidizing agents than ferric sulfate, among them silver nitrate and iodine in potassium iodide. The results from these methods were all low, indicating that some hydrogen must have been produced during the reaction.

After a long series of experiments it was found that the reducing power of the aluminum dust or flake on litharge, PbO, can be easily determined. It was found that the accuracy depended upon two factors: first, the formation of a liquid slag from which the globules of metallic lead could easily separate themselves; and second, the temperature at which the assay was run.

It was found convenient to make these assays in what are known as 25-g. fire-clay crucibles. A charge of 3 g. of metallic aluminum proved to be an appropriate amount for the determination. The aluminum is mixed with 100 g. of litharge and 30 g. of borax glass and a cover of 25 g. of borax glass is added. These proportions yield an amount of slag that is convenient to handle and of such a nature that it fuses readily to a very liquid mass, which can be easily and cleanly poured out of the crucible.

The fusions are conducted in a gas muffle heated to such a temperature that the dividing line between the end of the muffle and its bottom cannot be distinguished. The fusions require 20 min. after the crucibles are placed in the preheated muffle. After the fusions are complete, the molten mass is poured from the crucible into a conical slag mold such as is used by assayers. In these molds the molten lead settles to the bottom. After cooling, the lead bottoms break away easily from the slag, which is brittle, slightly yellow, almost transparent, and glassy in character.

Finally the lead bottoms are pounded into cubes to remove any adhering particles of slag and are then weighed. The accuracy of the results were found to depend upon the temperature at which the fusions were made. The requirements are that a high temperature should be used throughout, in order that the required time may be short, so as to minimize the reoxidation of the lead. According to the equation $2Al + 3PbO = Al_2O_3 + 3Pb$, the weight of the lead multiplied by the factor 0.0872 will give the equivalent weight of aluminum.

The following results were obtained on 3-g. samples of aluminum:

LEAD	ALUMINUM	
Grams	Grams	Per cent
33.580	2.9283	97.61
33.181	2.9489	98.29
33.645	2.9338	97.79
33.480	2.9195	97.32
33.683	2.9371	97.90
33.568	2.9271	97.57
33.567	2.9270	97.57

It should be noted that this method permits the use of a comparatively great weight of aluminum and further that the fact that the lead produced weighs nearly 12 times as much as the aluminum contributes to the accuracy of the results. The method is quick, easy, and accurate from a practical standpoint.

III—DETERMINATION OF NITRATES IN COMMERCIAL SALTS

At the present time the nitrates of potassium, barium, and strontium are extensively used in the manufacture of military pyrotechnics. A rapid and easy method for the determination of the pure nitrate content of the commercial salts depends upon the fact that when any of the above compounds are heated with an excess of tungstic anhydride (WO_3), oxygen and oxides of nitrogen empirically corresponding to N_2O_5 are liberated.

Gooch and Kurzirian[1] have shown that sodium paratungstate $Na_{16}W_{12}O_{41}$ has the property of decomposing nitrates. It was found on trial, however, that the use of tungstic anhydride gave better results owing to the fact that there was no loss by spattering during the fusion, a loss difficult to avoid if the paratungstate was used.

One gram of the nitrate is mixed in a platinum crucible with approximately 5 g. of tungstic anhydride, prepared by igniting tungstic acid in a platinum crucible with a good Bunsen burner for an hour, and subsequently kept in a desiccator over sulfuric acid. The mixture is heated carefully over a Bunsen burner, finally using the full heat of the flame. The reaction is generally complete within 10 min. From the loss in weight the percentage of the pure compound in the commercial sample is easily calculated.

This method was tested with carefully purified samples of potassium nitrate, barium nitrate, and strontium nitrate, yielding results within 0.05 per cent of the theorctical in each case.

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[1] *Am. J. Sci.*, [4] **31** (1911), 497.

THE APPLICATION OF THE ROTATING ZINC REDUCTOR IN THE DETERMINATION OF MOLYBDENUM

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Received January 5, 1920

INTRODUCTION

In former articles[1] results have been given showing the efficiency and rapidity of rapidly rotating metallic reductors in the reduction and determination of vanadic acid and ferric sulfate. In the present work a similar method has been applied to molybdic acid.

The reduction of molybdic acid by zinc is well known. Wernke[2] carried the reduction with zinc and sulfuric acid approximately to the condition of $Mo_{12}O_{19}$. Using the Jones reductor, Dudley[3] obtained slightly different results, while Jones[4] and Doolittle and Eavenson[5] obtained results similar to those of Wernke. Blair and Whitfield,[6] and Miller and Frank[7] obtained a reduction approximately **to** the condition of $Mo_{24}O_{37}$, while W. A. Noyes and Frohman,[8] by replacing air with carbon dioxide, got a degree of reduction corresponding to Mo_2O_3. Randall,[9] using ferric alum in the reducing flask and decolorizing with phosphoric acid according to Reinhardt[10] obtained a reduction to the condition of Mo_2O_3.

REDUCTION OF MoO_3 BY ROTATING ZINC CYLINDER

In all the following results the molybdenum has been estimated as MoO_3, the source of molybdenum being ammonium molybdate[11] which contained 81.35 per cent MoO_3.

Preliminary experiments showed that the rate of reduction at temperatures between 20° and 30° C. was nearly as rapid as when started at the boiling temperature of the solution, complete reduction being accomplished in about 5 min., for the amounts of MoO_3 taken. At temperatures below 20° C., however, the reduction was much slower.

In the first series of experiments, the results of which are shown in Table I, the reduction was brought about by a solid zinc cylinder into which was fixed an iron spindle attached to the shaft of a small motor which was run by the ordinary city current. When an electrolytic current was used, it was obtained from 8 storage cells. This cylinder was used in obtaining all the results which follow. A split cover-glass, in which a hole had been made slightly larger than the iron spindle, was placed over the top of the tall, narrow beaker during every reduction. After reduction the solution was poured into a larger beaker and the volume made up to about 350 cc. with ordinary distilled water (the solution changed from green to amber) and titrated with standard permanganate.

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[1] Gooch and Scott, *Am. J. Sci.*, **46** (1918), 427; Scott, THIS JOURNAL, **11** (1919), 1135.

[2] *Z. anol. Chem.*, **14** (1875), 1.

[3] *J. Am. Chem. Soc.*, **15** (1893), 519.

[4] *Am. Inst. Min. Eng.*, **18** (1889–90), 705

[5] *J. Am. Chem. Soc.*, **16** (1894), 234.

[6] *Ibid.*, **17** (1895), 747.

[7] *Ibid.*, **25** (1903), 919.

[8] *Ibid.*, **16** (1894), 553.

[9] *Am. J. Sci.*, [4] **24** (1907), 313.

[10] *Chem.-Ztg.*, **13** (1889), 323.

[11] Treadwell-Hall (3rd Ed. (1911), p. 284) states that molybdenum trioxide may be obtained from ammonium molybdate by heating carefully in a spacious crucible, finally to dull redness. The writer found that at very low redness a small amount of molybdenum trioxide always sublimed. This sublimation was overcome by thoroughly mixing the ammonium molybdate with 5 or 6 times its weight of acid tungstate of sodium, applying heat gently at first and finally to low redness. The anhydrous acid tungstate was prepared by adding tungstic trioxide to fused sodium tungstate. The composition of the tungstate was practically $Na_2W_2O_7$ or $Na_2O.2WO_3$.

A correction factor of 0.09 cc. of the standard permanganate has been applied to all the results recorded in this paper. This factor was determined under conditions exactly similar to those of the experiments.

TABLE I

Total volume of solution reduced, 53 cc.
Concentrated sulfuric acid, 5 cc. (or better, 10 cc. 1 : 1 acid)
Zinc surface in contact with solution, 70 sq. cm.

MoO_3 Taken G.	MoO_3 Found G.	Error G.	Time of Reduction Min.	Temp. before Reduction ° C.	Temp. at Titration ° C.	Volume at Titration Cc.	Rev. per Min.
A—PRELIMINARY							
0.0818	0.0313	—0.0505	1	21	18	350	700
0.0818	0.0488	—0.0430	2	22	20	350	700
0.0818	0.0612	—0.0206	3	21	20	350	700
0.0818	0.0713	—0.0105	4	22	21	350	700
0.0818	0.0720	—0.0098	5	21	21	350	700
0.0818[1]	0.0798	—0.0020	5	22	22	350	700
B—QUANTITATIVE							
0.0818	0.0723	—0.0095	4	Boiling	29	350	700
0.0818	0.0724	—0.0094	4	Boiling	28	350	700
0.0814	0.0702	—0.0112	4	Boiling	30	350	700
0.0818	0.0709	—0.0109	4	Boiling	29	350	700
0.0815	0.0705	—0.0110	5	22	23	350	700
0.0819	0.0704	—0.0115	5	22	24	350	700
0.0814	0.0704	—0.0110	5	22	22	350	700
0.0814	0.0716	—0.0098	5	22	23	350	700
0.0814	0.0705	—0.0109	5	22	24	350	700
0.0814	0.0697	—0.0117	5	22	23	350	700

[1] Reduced and titrated in same beaker.

These calculations are based on the assumption that the MoO_3 is reduced to Mo_2O_3. The low results indicate that oxidation had taken place, yet the color showed that the reduction was originally complete.

The last experiment in (A) would seem to indicate that if the solution were titrated in the same beaker in which it was reduced quantitative results might be obtained. Later experiments proved this to be true.

QUANTITATIVE DETERMINATIONS

REDUCTION AND TITRATION IN SAME BEAKER—In order to obtain quantitative results, as recorded in Table II, some care must be exercised to prevent oxidation and undesirable reduction.

1—The glass cover holds back enough hydrogen (from the action of sulfuric acid on zinc) to form a protective covering during reduction.

2—When reduction is complete, as indicated by the appearance of a dark green color, the cover is removed, and the zinc cylinder (rotating slowly) is raised out of the solution and water sprayed on it. The rotary motion of the cylinder throws the water against the side of the beaker and it runs down on the surface of the reduced solution without causing any stirring or mixing. This water being lighter than the reduced solution remains on top as a distinct layer, and forms a protective covering after reduction.

3—Small pieces of zinc are sometimes thrown off the cylinder and go into the solution. When this happens the solution should stand until the acid completely dissolves the zinc.

4—It seems advisable to allow the hydrogen in the solution to collect in bubbles. These may be removed by slight jarring or by slowly moving a glass rod along the side and bottom of the beaker.

5—The permanganate is run into the beaker, and with careful stirring the reduced molybdenum solution need not come into contact with the air until about the Mo_5O_8 stage, when the oxidizing effect is negligible.

Except where specified, the conditions of reduction are the same as in Table I.

When reduction was started at room temperature the solution warmed up 6° or 8°; when started at the boiling point the temperature at the end of the reduction was 70° to 80°.

TABLE II

MoO_3 Taken G.	MoO_3 Found G.	Error G.	Time of Reduction Min.	Temp. before Reduction	Temp. at Titration ° C.	Volume at Titration ° C.	Revolutions per Min.
A—Reduction Started at Boiling; Zinc Washed with Distilled Water							
0.0818	0.0808	—0.0010	4.5	Boiling	21	100	700
0.0814	0.0809	—0.0005	4.5	Boiling	21	100	700
0.0819	0.0809	—0.0010	6.5	Boiling	20	100	700
B—Reduction Started at Boiling Temperature; Zinc Washed with Freshly Boiled Distilled Water							
0.0815	0.0807	—0.0008	4	Boiling	50	100	700
0.0819	0.0813	—0.0006	4	Boiling	55	100	700
C—Reduction Started at Room Temperature; Zinc Washed with Distilled Water							
0.0818	0.0810	—0.0008	6	20	27	100	700
0.0817	0.0817	—0.0010	5	21	28	100	700
0.0817	0.0805	—0.0012	5	22	28	100	700
0.0817	0.0810	—0.0007	5.5	20	28	100	700
D—Reduction Started at Room Temperature; Zinc Washed with Freshly Boiled Distilled Water							
0.0817	0.0812	—0.0005	5.5	21	31	100	700
0.0816	0.0818	+0.0002	5	21	30	100	700
E—(Quantitative) Reduction at Room Temperature; Zinc Washed with Freshly Boiled Distilled Water							
0.0816	0.0820	+0.0004	5.5	20	28	100	700
0.0818	0.0821	+0.0003	5.5	22	30	100	700
0.0818	0.0821	+0.0003	5.5	21	25	100	700
0.0819	0.0821	+0.0002	5.5	20	31	100	700
0.0816	0.0817	+0.0001	5.5	22	27	100	700

Table II shows that the best results were obtained when reduction was started at room temperature and the cylinder washed with distilled water which had been freshly boiled.

REDUCTION BY ROTATING ZINC ANODE—The results in Table III were obtained by making the zinc cylinder the rotating anode and a piece of platinum 5 by 10 cm. the stationary cathode. Otherwise the conditions were the same as in Table II-E.

TABLE III

MoO_3 Taken G.	MoO_3 Found G.	Error G.	Time of Reduction Min.	Temp. before Reduction ° C.	Vol. at Titration Cc.	Rev. per Min.	Current Used Amp.
A—PRELIMINARY							
0.0814	0.0516	—0.0298	1	22	150	700	6
0.0814	0.0670	—0.0144	2	22	150	700	6
0.0814	0.0775	—0.0039	3	22	150	700	6
0.0814	0.0812	—0.0002	4	22	150	700	6
B—QUANTITATIVE							
0.0815	0.0813	—0.0002	4.5	22	150	700	6
0.0815	0.0811	—0.0004	4.5	21	150	700	6
0.0816	0.0814	—0.0002	4.5	23	150	700	6
0.0814	0.0811	—0.0003	4.5	21	150	700	6

These results show that the reduction, when the electrolytic current was used, was brought about in a little less time than when no electrolytic current was used.

DETERMINATION OF MOLYBDENUM USING IRON SOLUTION—The results in Table IV were obtained by reducing the molybdenum by the rotating zinc cylinder (no electrolytic current) and then pouring the reduced solution into a beaker containing ferric alum and phosphoric acid (25 cc. ferric alum solution, made by dissolving 100 g. ferric alum in 1 liter of water; 5 cc. sirupy phosphoric acid).

TABLE IV

MoO_3 Taken G.	MoO_3 Found by $KMnO_4$	Error G.	Time of Reduction Min.	Temp. before Reduction ° C.	Vol. at Titration Cc.	Rev. per Min.
0.0815	0.0818	+0.0003	5.5	25	400	700
0.0818	0.0818	0.0000	5.5	30	400	700
0.0816	0.0811	—0.0005	5.5	23	400	700
0.0819	0.0812	—0.0007	5.5	22	400	700
0.0816	0.0814	—0.0002	5.5	22	400	700
0.0815	0.0815	0.0000	5.5	21	400	700
0.0814	0.0810	—0.0004	5.5	22	400	700

The above results show that the reduced molybdenum solution may be titrated in a separate beaker from that in which it was reduced, provided the mixture of ferric alum and sirupy phosphoric acid is used to effect the preliminary oxidation of the molybdenum while in the very sensitive stage.

CONCLUSIONS

The foregoing results show that molybdic acid in dilute sulfuric acid solution may be reduced by a rotating zinc cylinder, either with or without the aid of the electrolytic current, when certain precautions have been observed; also that when ferric alum and sirupy phosphoric acid are added immediately to the reduced molybdenum solution, the titration may be made in a separate beaker from that in which reduction is brought about.

The molybdic acid may be determined quantitatively in all cases by titrating the reduced solution with standard potassium permanganate.

The above processes may be advantageously used in place of the ordinary Jones reductor, after interfering substances have been previously removed by any of the ordinary methods. Assuming ammonium phosphomolybdate to have the composition $(NH_4)_3PO_4.12MoO_3$, P or P_2O_5 may be indirectly determined by this method.

It might also be added that when the work on this series of articles terminated, the writer was working on a volumetric method for the determination of tungsten (or tungsten trioxide) and had succeeded in keeping it completely in solution practically to the WO_2 stage. This process will be further investigated at some future time.

ACKNOWLEDGMENT

This work was done in the Kent Chemical Laboratory of Yale University in 1918, and the writer wishes to thank Professor F. A. Gooch, whose interest was stimulating and kindly advice most helpful at all times.

A RAPID METHOD FOR QUANTITATIVE DETERMINATION OF ARSENIC IN COMMERCIAL SULFURIC ACID

By A. A. Kohr

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Received January 29, 1920

In various commercial operations where sulfuric acid is used, an acid of low arsenic content is often desired. A situation arose at this plant not long ago demanding that the arsenic content of each shipment of acid be determined before the shipment was received.

The literature on this subject was accordingly examined, and various methods tried, but all proved laborious and time-consuming. Some of the methods involved the reduction of the arsenic in the arsenic form, some a precipitation with hydrogen sulfide, and some both of these procedures. The ones giving the best results were the most time-consuming, the operation requiring the greatest amount of time being the reduction of the arsenic form.

It was thought, accordingly, that a method involving the determination of each form of arsenic separately would be very advantageous. The determination of arsenious arsenic presented no particular difficulty, as a slight modification of one of the standard methods would suffice. The method for the determination of each form finally adopted is given below.

METHOD

ARSENIOUS FORM—Weigh out 20 g. of acid and dilute with a small amount of distilled water, and add a few drops of methyl orange indicator. Carefully neutralize with a saturated solution of sodium carbonate until the methyl orange shows a very faint pink (about one drop more would turn the solution completely yellow), and add about 2 g. of sodium bicarbonate powder in excess. Make up solution to about 250 cc. with distilled water, if necessary, and titrate with 0.1 *N* iodine solution, using starch as an indicator. A blank determination should be made on the reagents and suitable correction made.

Cc. 0.1 *N* iodine × 0.00495 = g. As_2O_3 in the arsenious form.

ARSENIC FORM—Weigh out 20 g. of the acid to be tested into a small beaker, and place in an oven regulated at 105° to 110° C. for about an hour. Dilute with a small amount of distilled water, and add a saturated solution of sodium carbonate until just in excess (red color with phenolphthalein). Boil, and filter into an Erlenmeyer flask. Wash thoroughly and add about 3 g. sodium bicarbonate powder, add 150 cc. strong hydrochloric acid slowly with occasional agitation, then add about 1 g. potassium iodide crystals, and cover the flask to keep out air. Agitate and then allow to stand 5 min. Titrate the iodine liberated with 0.1 *N* thiosulfate, with starch as indicator.

Cc. 0.1 *N* thiosulfate × 0.00495 = g. As_2O_3 in arsenic form.

Arsenic in arsenic form + arsenic in arsenious form = total As_2O_3.

Total $As_2O_3 \times 5$ = per cent total As_2O_3.

Per cent total $As_2O_3 \times 0.7575$ = per cent total As.

DISCUSSION

$$H_3AsO_3 + I_2 + H_2O \rightleftarrows H_3AsO_4 + 2HI$$

The above reaction proceeds from left to right when the hydrogen-ion concentration is low, and there should be very few OH ions. Excess sodium bicarbonate does not interfere. In the presence of sufficient hydrochloric acid the reaction goes from right to left. It is quantitative in both directions.

Salts of copper interfere in the above determination of the arsenic form of arsenic, but in most cases the copper content will be low enough to be negligible. Should copper be found in an appreciable quantity, however, it should be determined and a correction applied to the thiosulfate titration, remembering that each mole of copper will liberate one mole of iodine from potassium iodide. If copper is present in any quantity the amount of potassium iodide added should be increased accordingly. The only other constituents likely to interfere with the determination of the arsenic form have been removed by the method of procedure. Nitrous and nitric acids would be volatilized during the heating. Ferric iron would be precipitated by the sodium carbonate and removed in the subsequent filtration.

This method has been checked against various other arsenic methods and results have been found to agree very well. Duplicate determinations of the same acid have been found to check closely.

LABORATORY AND PLANT

SEED-CULTURE METHODS IN THE PRODUCTION OF ACETONE AND BUTYL ALCOHOL BY A FERMENTATION PROCESS

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Received January 15, 1920

A bacteriological fermentation process may be divided for descriptive purposes into two parts: firstly, the preparation, fermentation, and distillation of the large bulk of raw material; and secondly, the preparation, in an active and pure condition, of the necessary volume of culture, to act as seed-culture for the final fermentation. In a previous article[1] an outline was given of the essential features of a plant concerned in the first of these divisions of the process. In the present communication it is proposed to consider the apparatus and methods of working in the production of seed.

Emphasis must be laid in the first place on the necessity of an adequately equipped laboratory. Furthermore, the principles of bacteriology must be allowed to control and direct not only the laboratory, but the operations of the entire plant.

The problem consisted in finding the best method of developing from a laboratory tube culture a sufficiently large and active volume of culture to start a fermentation in a large fermenter, containing 24,000 gal. of mash, which will occupy the minimum number of hours and give the maximum yield of products. Such questions as the following at once arose:

(1) What is the correct ratio between the volumes of the seed-culture and the mash to be inoculated?

(2) At what stage in the fermentation must the culture be used as seed?

(3) Can the organism growing in maize mash be subcultured indefinitely in the same type of medium without loss of vitality? If not, what is the number of generations between the tube and the fermenter which will insure the maximum efficiency in the latter?

Because the great demand for acetone made impossible small-scale, preliminary experiments, these questions were answered in the factory rather than in the laboratory. The seed plant was often modified, and, when the armistice was signed, it represented the sum of the experience gained during the previous two and a half years.

The second question will be considered in detail. During the fermentation the acidity of the mash rises steadily for about 15 hrs. and then falls for about the same number of hours. In all stages of the seed process the culture was transferred to the next batch when the acidity had just begun to fall, for the following reasons: At this point the organism had ceased dividing and had passed through the chain stage. The medium, however, had not yet separated into a clear fluid with a slimy floating head which contained the majority of the bacteria, but was still homogeneous and contained the maximum number of free motile organisms. In this condition the culture could be divided equitably between several batches of mash. It was also found that when contamination occurred only one species of foreign organism developed, and this type was responsible for the stoppage of the fermentation. In the early stages the contamination could not be detected by its morphology or by chemical tests, but toward the end of the fermentation the contamination stood out clearly in faintly stained preparations, and the acidity of the mash did not fall but rose to a very abnormal maximum. For these reasons it was considered advisable to wait until the acidity had commenced to fall, and until slides had been examined very carefully, before passing the culture into a larger volume of mash.

A further question arises in connection with the number of vessels to be included in the system. Supposing that 1,000 gal. of culture are required each day for four large fermenters, is it advisable to prepare this in one or more vessels? If one vessel is used there is a saving in time and labor, and, what is of greater importance, by reducing the number of pieces of apparatus to the minimum the danger of contamination is correspondingly reduced. On the other hand, if contamination does occur, the plant may be idle for a day. Furthermore, while in general it is possible to arrange that the culture be in the right condition when required, occasional delays may occur or the fermentation may be unusually rapid. The operator must then divide among four fermenters the 1,000 gal. of culture which have separated into clear beer and head. Not only is this almost impossible, but often the head refuses to pass out of the seed vessel along the lines, and the fermentations are slow in the fermenters. As far as possible, therefore, the culture for each final fermentation represented a complete smaller-volume fermentation.

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[1] Speakman, *J. Soc. Chem. Ind.*, **38** (1919), 155.

MECHANICAL DETAILS OF THE PLANT

MATERIAL—The seed plant as a whole was composed of copper vessels. In many cases it was found that the first fermentation in a new vessel was slow and incomplete, and upon examination of the interior the bright metallic surface was found tarnished by thin deposits of some unknown, dark substance. If this thin layer were removed and a new surface of metal exposed, the same result was obtained when the tank was used again. The vessel should therefore be washed out but not scoured. It is suggested that the thin deposit over the copper reduces the action of the fermentation acids on the metal, and thus diminishes the formation of toxic metallic salts. Aluminum vessels have been used with success in England, but from the bacteriological standpoint they offer no advantages as compared with copper vessels, and from the mechanical standpoint they are much inferior.

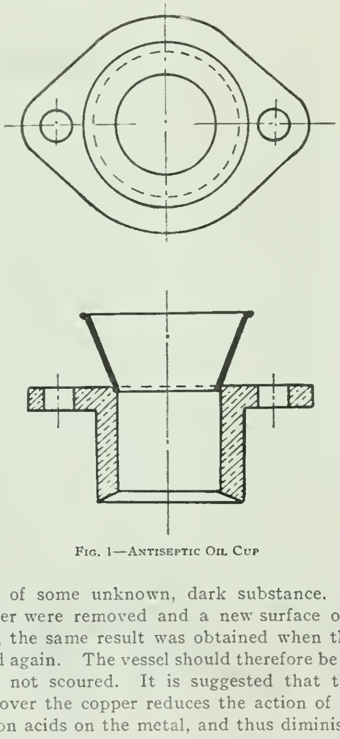


FIG. 1—ANTISEPTIC OIL CUP

SITUATION—The vessels should be so arranged in relation to one another, that the culture can flow by gravity with fair rapidity from one stage to the next. This arrangement obviates the use of pumps in the seed lines, which is a great help in the preservation of sterility. If pumps are required it is advisable to use the rotary type and they should be completely immersed in baths of dilute carbolic acid.

STERILITY DEVICES—Certain mechanical devices to preserve sterility were used on all the vessels. The drains from the lines were of the type previously described. To provide for agitation of the mash during the various operations a central shaft passed through a gland in the domed roof and was supported by a step bearing on the bottom of the vessel. To prevent contamination through the gland a cup was brazed on the top of the latter (Fig. 1). During the cooking and cooling periods this cup was filled with a mobile mixture of grease, butyl alcohol, and carbolic acid, which worked down into the gland and acted as a lubricant, while the excess in the cup indicated whether the gland was leaking when the vessel was under pressure. In this indirect way, and by preventing to some extent the passage of air into the vessel during the cooling period, the cup helped to eliminate this source of contamination.

Another fruitful source of trouble was the gauge glass. Those originally placed on the fermenters were removed, but the gauge glass was an essential part of the equipment of the smaller vessels. In order to increase their usefulness and lessen the danger, large brass mountings were designed for all the vessels. Instead of the usual narrow bore of steam mountings, one which was half an inch in diameter was called for, to prevent the closing up of the valves with mash. If this did occur the glass and fittings could be cleaned out with steam. Owing to the structure of the gauge-glass valves there is always a danger that leaks will develop around the spindle, and they were accordingly assumed to be always in this condition. A low-pressure steam connection (Fig. 2) was made in the upper valve.

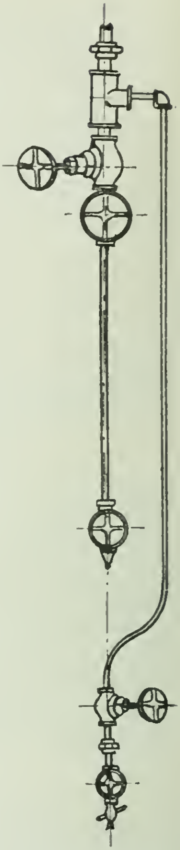


FIG. 2—GAUGE GLASS AND SAMPLING COCK

During the cooking and fermentation periods the valves were open and the steam connection valve was closed. The tank was under steam or gas pressure during these periods. During the cooling period and early hours of the fermentation, the top valve was closed and a slight amount of steam was turned on. After the condensed steam in the line washed out the glass, the bottom valve was closed, steam still being turned on. The gauge glass gradually filled with sterile water under a slight pressure and the passage of air into the tank through the gauge valves was prevented.

A sampling cock was also part of the necessary equipment, and likewise a source of anxiety and trouble. In addition to the usual danger of leakage, there was also the difficulty that when samples were withdrawn from the vessel during the fermentation, slight deposits remained on the inside of the cock below the plug. These deposits contained a large number of bacilli. Although during the next cooking period the deposits dried and the organisms were doubtless killed by conducted heat, this could not be depended upon. At the close of the cooking period a sample of the mash was examined under the microscope. If organisms were to be seen in the preparation, the only safe thing to do was to cook the mash further. In this way valuable time was lost. To prevent leakage the cocks were examined each day, and to eliminate as far as possible the trouble in connection with the sterility test the following steps were taken: In the interim between the emptying and filling of the vessel, a slight amount of steam was kept passing into it. The valves and cock were partially closed and at intervals they were all closed for a few minutes. When pressure developed the valves were opened in turn and the steam allowed to rush through them to thoroughly clean the body of the valve. When the tank was once more full the cock was cleaned out with cotton-wool soaked in dilute carbolic acid, and plugged with a clean piece of cotton.

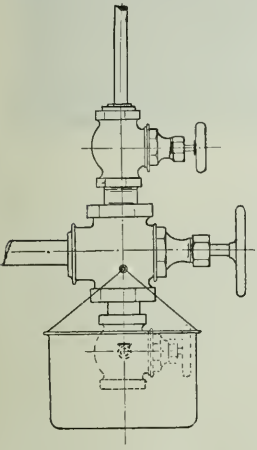


Fig. 3—Sampling Cock

In Fig. 3 are given the details of a sampling cock which was tried with success on one of the seed-vessels at the close of 1918. The main portion of the apparatus was an ordinary one-half inch cross-valve, the whole body of which could be thoroughly cleaned and sterilized with steam. During the cooking period and between the taking of samples the whole of the valve on the discharge side was full of condensed steam under pressure. The small cock was cut down below the plug. As an extra precaution the cock was immersed in a cup of antiseptic, suspended from the valve above. This valve should eliminate sources of contamination, causes of delay, and also tedious operations.

LABORATORY CULTURE METHOD

The starting point in the preparation of the seed was a test tube containing the products of a fermentation, maize residues, and spores of the bacillus (Fig. 4). The tube had been stored for 3 mo. in a cool, dry place after the fermentation ceased. In the earlier stages in the development of the process the tubes were immersed in boiling water for 0.5 to 1.5 min. just previous to use. This technique resulted in a gradual improvement in the laboratory stock and increased yields in the plant. Two 12-in. tubes, constricted in the middle, and containing 10 cc. of mash, were inoculated with 2 cc. of the contents of one of these spore tubes. The latter should not be shaken and as far as possible the maize residues should be taken up into the pipette, since the majority of the spores are embedded in the spongy mass. After inoculation the plugs of the tubes were pushed down to the constriction and the part above the plug was drawn out to a capillary in the middle, using the blow-pipe flame. The tubes were then evacuated and sealed off. At the end of 24 hrs. there was usually a considerable pressure in the tubes, due to the germination of the spores and the development of a vigorous fermentation. The more active tube was opened above the plug. From this five open test tubes containing 10 cc. of 5 per cent mash were inoculated, adding 1 cc. of culture to each tube, and incubated at 37° C. Although we were dealing with an anaërobic organism, an evacuated desiccator was not used. If the inoculant was placed at the base of the starch gel and the tube was not shaken, bubbles of gas very soon surrounded the culture and gradually created throughout the whole tube an anaërobic atmosphere. The success of this operation depended on the vitality of the bacillus, and more specialized technique must be adopted when sluggish cultures or spores are used. On the following day two of the tubes were used to inoculate two 500-cc. Erlenmeyer flasks containing 300 cc. of 5 per cent mash (Fig. 4). The remaining tube cultures were incubated for two more days and, if necessary, were then used to maintain the stock of spore tubes.

Fig 4—Laboratory Cultures

Smears of the cultures were made, converted into permanent preparations, and labeled for future reference. An important feature of the system was that a new culture was started each day and became the starting point for the whole of a later day's factory operations. The minimum amount of subculturing was done in the laboratory, and consequently the

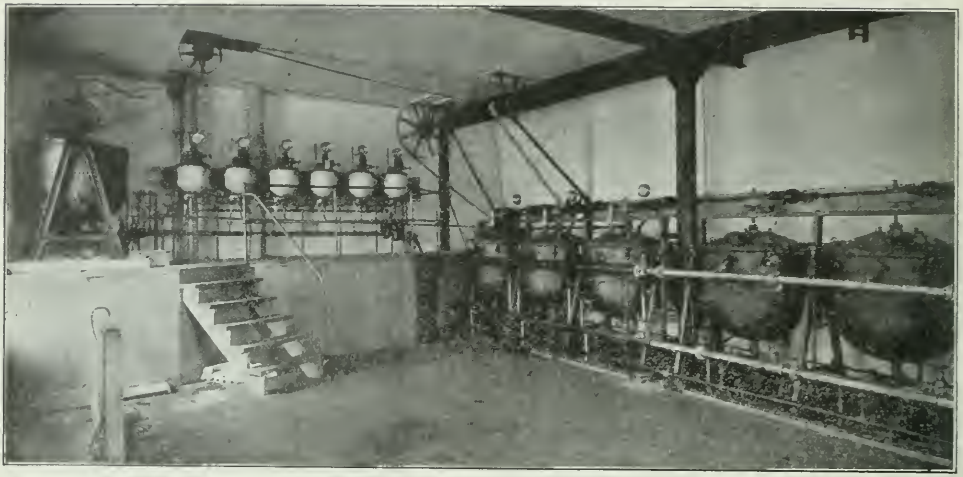


Fig. 5—Inoculator Room

danger of slow fermentations in the factory was reduced to a minimum. It was found impossible to predict from the morphological characteristics of the organism in the early laboratory cultures what the final fermentation would be; therefore, the number of generations between the spore culture and the fermenter must be reduced to the minimum. It is believed that it was largely due to the adoption of this system that the time of the final fermentation period was reduced in 2 years from an average of 48 hrs. to an average of 30 hrs.

CULTURE-VESSELS AND INOCULATORS

We now pass from the laboratory to the factory. In Fig. 5 two batteries of fermentation vessels are shown. The group of smaller ones fixed on the far wall were named "culture-vessels," and the larger ones to the right, "inoculators." The third size of vessel used in the development of the seed was given the more familiar name, "seed-tank."

Culture-Vessel Construction

Material: 16 gauge copper

Dimensions: 13 in. diameter × 12 in. deep, with hemispherical steam-jacketed bottom and flanged domed cover

Capacity: 5 gal.

Stirring Gear: 16 × 3 in. paddle stirring gear driven by hand through bevel gears, and horizontal handle

Equipment: 0.5 in. globe valve for air or gas; 1 in. gate valve for filling; 1 in. outlet; 250° F. canners' thermometer; 30 lb. 30 in. pressure-vacuum gauge; 0.5 in. sampling cock

Jacket Connections: 0.5 in. connection at the top for inlet steam or outlet cooling water; $^3/_8$ in. connection at the base for condensed steam outlet or cooling water inlet; pet-cock drain in the bottom of the jacket

Inoculator Construction

Material: 16 gauge copper

Dimensions: 3 ft. diameter × 2 ft. 7 in. deep, with hemispherical steam-jacketed bottom and 6 in. flanged domed cover

Capacity: 95 gal.

Stirring Gear: A 4 ft. 6 in. shaft $1^3/_{16}$ in. thick projected through the cover and carried a screw propeller 9 in. from the bottom; the mash was thrown upwards; the shaft was belt driven with counter shaft and pulleys at 88 r. p. m.

Equipment: The cover was provided with flanged connections for the following: 15 lb. 30 in. vacuum-pressure gauge, 260° F. mercury thermometer, 1.5 in. gate valve for air inlet, 4 in. diameter screwed cover handhole, fitted with rubber washer. In the side of the tank above the jacket was a 0.5 in. sampling cock and a 0.75 in. gauge glass with a lower connection in the exit line (Fig. 6)

Pipe Connections: (*a*) 1.5 in. connection in the cover to the culture-vessels

(*b*) In the side of the vessel at the front a 2 in. connection to the filling line

(*c*) In the jacket a 1 in. water inlet and exit for the condensed steam and a similar connection for the steam inlet and water overflow; also a $^3/_8$ in. air vent in the jacket

PREPARATION OF THE MASH

On the left of the culture-vessels in Fig. 5 can be seen an open vessel in which the mash for the vessels in this room was prepared. The detail of this vessel was as follows:

Material: 16 gauge copper

Dimensions: 3 ft. 2 in. diameter × 2 ft. 8 in. deep with hemispherical steam-jacketed bottom

Capacity: 100 gal.

Stirring Gear: A central shaft was equipped with two paddles rotating in a clockwise manner, and a scraper rotating in a counter clockwise manner. These were belt driven through bevel gears and pinion at 11 r. p. m.

Steam Supply: These connections were similar to those for the inoculators

Drain: The 2 in. drain connection discharged into the line to the inoculators or into the metal tray under the vessel

A charge of 80 gal. of mash was made twice each day. The water was run into the open vessel from an overhanging line, and during this operation, with the gear in motion, the meal was evenly shaken by hand into the water from a sack. It is advisable not to turn on steam until the meal and water are thoroughly mixed. When the mash is approaching the boiling point it is liable to flow over the sides of the vessel, and steam must be carefully controlled.

CULTURE-VESSEL OPERATIONS

When the vessel was not actually in use, a small quantity of steam was passing into it from a small jet tapped into the drain connection above the valve. The jet inside the line was turned downwards so that the steam played on the valve gate. After draining the vessel 3.5 gal. of mash were measured from the charge in the open vessel and poured by hand into the culture-vessel. The vessel was slowly raised to 10 lbs. steam pressure, using the jacket. At intervals a quick shot of steam was blown through the jet above the drain valve. This prevented the formation of hard deposits of mash in the vertical piece of line above the valve. Agitation by the hand-gear was not necessary to keep the mash in circulation during the cooking period. At the end of 2.5 hrs. a sample of the mash was examined under the microscope in the laboratory. After 3 hrs. cooking the mash was cooled to 98° F., and during this 30 min. period the hand-stirring gear was used. The vessel was then inoculated with one of the flasks previously described, containing 300 cc. of culture. All the valves were closed after the inoculation, and remained so until a pressure of about 2 lbs. was created in the vessel by the production of gas. The small valve in the cover was then adjusted to keep this pressure approximately constant. The filling and gas valves were still covered with pads. At intervals of 2 hrs. during the fermentation period samples of the culture were examined in the laboratory A slide was made and examined, and the acidity of a 10 cc. sample was determined by titration with 0.1 *N* sodium hydroxide. Each hour the temperature of the vessel was recorded, also the times at which the temperature was adjusted, and the temperature before and after this operation. Whenever it became necessary to account for abnormalities in the fermentation it was of great advantage to be able to eliminate the possibility of temperature variation. No attempt was made to measure the production of gas. A careful record was made of the times of filling, cooking, etc., and duplicated in the laboratory.

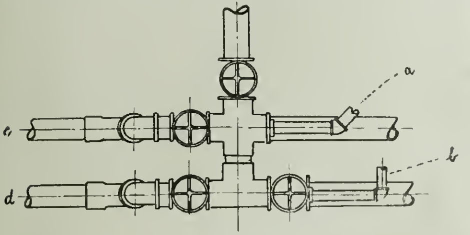


FIG. 6—PLAN OF SEED-TANK SYSTEM OF PIPING: *a*, STEAM SUPPLY; *b*, DRAIN; *c*, EMPTYING LINE; *d*, FILLING LINE

INOCULATOR OPERATIONS

The remainder of the charge of mash was allowed to flow by gravity into the inoculator which had been previously washed out and maintained while empty at 212° F. The mash was cooked as described above and cooled to 98° F. During the cooking period the body of the air valve, *i. e.*, above the gate, was filled with dilute carbolic acid which was raised to the boil. During the cooling of the vessel a large pad was securely tied over the valve and air allowed to filter through into the vessel.

The six culture-vessels drained into a common header made of 1.5-in. copper pipe. The line had a gentle slope towards the inoculators and ran the length of the battery, being connected to each inoculator by a vertical length of the same material. The connection to the inoculator was controlled by a globe valve (see Fig. 5). When the line was not in use for the passage of culture it was under steam pressure. The top end, *i. e.*, to the left of the culture-vessels, was connected to a small cylinder fitted vertically on the wall. The cylinder had been made from 4 ft. of 6-in. iron pipe and screw caps. In the top cap there was a connection to the low-pressure steam supply, and the bottom connection drained into the copper line. There was also a steam gauge glass extending the length of the cylinder. When the line was not in use the cylinder was cut off, and the steam passing into it gradually condensed and filled the container with sterile water at practically room temperature.

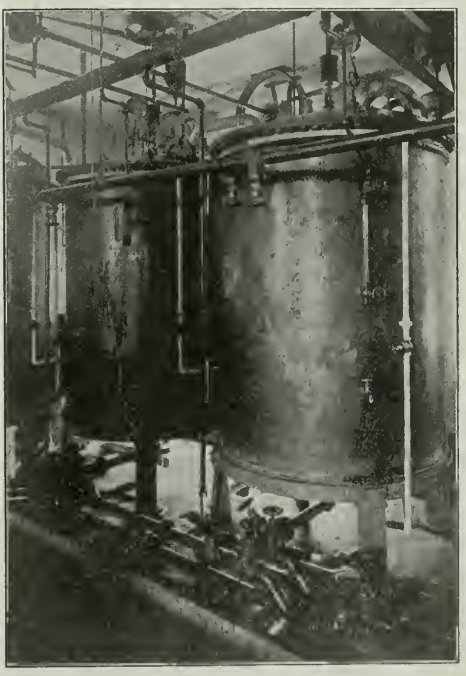


FIG 7—SEED-TANK

To transfer the contents of a culture-vessel to an inoculator the copper line was drained and steam-sealed. The control valve on the line to the particular inoculator was opened; the air valve was already padded and open. A charge of the cool, sterile water was passed along the line into the inoculator in order to cool the line and safeguard the comparatively small volume of culture to be transferred. The water supply was then cut off and the culture-vessel was allowed to empty into the lower vessel. The line was washed out with the remainder of the sterile water and again put under pressure.

Immediately after inoculation the mash was thoroughly mixed and all valves closed until the gauge showed that the fermentation had begun. A slight pressure was maintained in the vessel by regulating the flow of gas through the large air valve.

During the fermentation period the culture was examined microscopically and the acidity determined at regular intervals. The records were kept in the manner previously described.

SEED-TANKS

The battery of sixteen seed-tanks (Figs. 6 and 7) was situated on the floor immediately below the room containing the smaller vessels, and 15 ft. above the fermenters. The following were the main mechanical features of the tanks:

Dimensions: 4 ft. 6 in. × 6 ft. 6 in. deep, cylindrical in form with domed cover and dish bottom

Capacity: 628 gal.; 500 gal of mash when in operation

Fittings: The cover was provided with flanged connections for the following: 15 lb. pressure vacuum gauge, 2 in. gate valve for use as air inlet, 1 in. gas outlet, and in the cover there was also a manhole. In the side there was an upper and lower angle thermometer, a sampling cock, and a gauge glass covering the upper levels

Stirring Gear: The central shaft passing through the cover was supported at the base and at the ceiling by step bearings. On the shaft at the base there was a 10 in. diameter by 5 ft. 0 in. pitch propeller set to throw the mash downwards. Above the propeller were two stationary baffles riveted across the tank, the one above the other. Between the baffles there was a single, tapering blade fastened to the central shaft. The baffles prevented the agitated mash from moving in a body. The shaft was belt-driven from a counter shaft

System of Piping: (*a*) *Filling and Emptying:* The single opening in the center of the base was connected by a group of fittings to both the filling and emptying lines (Figs. 6 and 7). These lines ran parallel around the inside of the rectangle formed by the tanks. The horizontal pipe from the outlet passed through a control gate valve to the front, through a cross fitting above the emptying line, and then into a tee fitting above the filling line. The cross and tee were connected to the two lines by a gate valve, 45° angle and Y-fittings with close nipple connections. The remaining opening in the cross was connected to the low pressure steam supply and the third opening of the tee opened through a valve on to the tray below the tank

(*b*) *Inoculator Connection:* The culture from upstairs passed into a horizontal system of piping running around the inside of the rectangle, about 6 in. from the top of the tanks. Each seed-tank was connected by a short valve-controlled fitting to this line. The steam for sterilizing the line was supplied at the far end upstairs, and in the seed tank room two steam-sealed drains ran down to the tray

(*c*) *Gas Discharge:* The seed-tanks were divided into groups of four. Above each group there was a horizontal cross connection of 1.5 in. pipe, with vertical connections to the several tanks. From the pipe system a connection ran to a specially designed antiseptic seal (Fig. 8). When gas passed through the seal a pressure equal to approximately 12 in. of water was maintained in the seed-tank. No attempt was made to measure the volume of gas given off

Usually the tanks were filled in groups, and when not in use the whole of the gas piping was under steam pressure with the tank connection valves closed

(*d*) *Cooling System:* The mash was cooled by an even curtain of water discharged from a covered ring fitted around the top of the tank just below the flange

SEED-TANK OPERATIONS

When not in use the tanks were maintained at 212° F., with a little steam blowing through the air valve and sampling cock. Before being used again the tank was carefully examined by a competent mechanic.

FILLING—The mash for the seed-tanks was forced upstairs from the fermenter floor by the pressure maintained in the cooker, *i. e.*, 10 to 15 lbs. Owing to the design of the filling connection, the filling of the tank was not attended by the noise and shaking of the plant which occurred when the mash discharged into the tank through a side connection 4 ft. from the floor. In addition the mash did not froth so much when the tank was almost full and the height could be read with much greater accuracy in the gauge glass. The filling of each tank occupied 20 min.

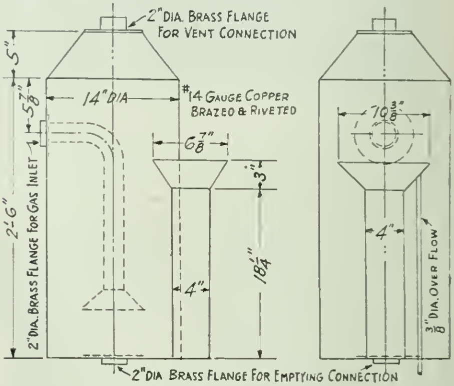

2" DIA. BRASS FLANGE FOR VENT CONNECTION
5"
5 7/8"
14" DIA
#14 GAUGE COPPER BRAZED & RIVETED
6 7/8"
3"
2'-6"
2" DIA. BRASS FLANGE FOR GAS INLET
18 1/4"
4"
10 3/8"
4"
3/8" DIA. OVER FLOW
2" DIA BRASS FLANGE FOR EMPTYING CONNECTION

Fig. 8—Detail of Gas Seal

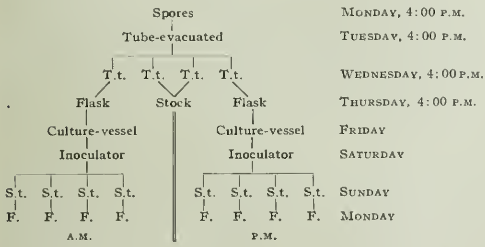
COOKING—The steam supply for the cooking of the mash passed through the horizontal bottom connection. This method obviated the danger of hard mash settling in the line and causing trouble by remaining unsterilized or blocking the line when the culture was required for a fermenter. The only way in which the line could then be cleared was by allowing steam to pass along the line from the emptying line which was under pressure, which was a very risky operation. This difficulty often arose when the steam supply passed through two separate nozzles in the bottom of the tank. Furthermore the supply of steam used in the cooking operation could also be used to create a seal of sterile water between the nest of valves in front of the tank. This seal prevented the possibility of contamination due to leaking valves.

COOLING—When the mash had been cooked for 2 hrs. and had been found satisfactory by examination in the laboratory, it was cooled down to 98° F. in the manner previously described. Below 212° F. air was allowed to pass into the tank through the air valve, which had been thoroughly sterilized by being filled with dilute carbolic acid during the cooking period.

INOCULATION—Each of the four tanks filled together was given an equal share of the contents of an inoculator which were about 18 hrs. old. After inoculation the tank valves were all closed. When one of the tanks showed a gauge pressure of 2 lbs. the seal was emptied and refilled with fresh carbolic solution. The steam to the gas line was then cut off, and the gas from the most active seed-tank allowed to bubble through the seal. As the fermentations developed, the tanks were in turn connected to the gas line.

FERMENTATION—During the fermentation period samples of the culture were examined at regular intervals in the laboratory. The culture, when about 18 hrs. old, was used as seed for a fermenter. It was allowed to flow by gravity into the mash-filling line to the fermenters, entering the line just beyond the point where the cooler discharged into the line. The connection was carried through into the larger line and turned against the stream of mash. In this way the seed was thoroughly mixed with the much larger volume of mash. The contents of one seed-tank, 500 gal., were used to inoculate a fermenter containing 24,000 gal. of mash. This was made possible by filling the fermenters in the manner described elsewhere.

SUMMARY—The whole of these operations are summarized in the following table, which shows that each day eight stages had to be prepared and controlled.



RECORDS

Mention has already been made of the recording of operations in the plant and observations in the laboratory. In addition, the following method was adopted to assist in studying the causes of poor fermentations, due to the weakness of the culture itself or to contamination. Previous to using any fermentation as seed, the last of its series of slides was made into a permanent preparation and labeled. A sample of the culture was collected in a large, sterile test tube and incubated. The sample and slides were kept until the corresponding fermenter had been distilled and the yields of acetone and alcohol calculated. Supposing that a particular fermenter was not up to the average it was not an easy task to go back over the eight stages, involving the use of several vessels, and locate the source of the trouble. The task was made easier by the fact that it was possible to return to the sample and slides. If contamination had occurred in any stage the corresponding sample would by that time have a very high acidity, and very possibly smears would indicate directly the presence of the contamination. Not only were mechanical faults discovered in this way but also the personal factor was eliminated wherever possible.

I wish to acknowledge the assistance received from the members of the staff of the Fermentation Department during the erection and operation of the seed plant.

MEASUREMENT OF VISCOSITY OF PYROXYLIN SOLUTIONS[1,2]

By E. F. Higgins and E. C. Pitman

E. I. du Pont de Nemours & Co., Wilmington, Del.

Received October 15, 1919

INTRODUCTION

The accurate control of the viscosity of pyroxylin solutions is of importance in nearly all industries making use of soluble cotton products. It is of value to the manufacturer to have one instrument which can be used for his entire range of solutions of both high and low viscosities, so that all his results may be expressed in units which are directly comparable.

The object of this investigation was the comparison of a number of commonly used types of viscosimeters, with respect to accuracy, facility of manipulation, and range over which they could be used to advantage. Although it is the usual industrial practice to express viscosity as compared with some standard liquid, or as a purely empirical number, *e. g.*, in seconds, we have calculated from our data absolute viscosities as well, in order that direct comparisons may be made between the various instruments.

EXPERIMENTAL DETAILS

Comparisons of the following viscosimeters were made:

A—100 cc. outflow pipette
B—Tagliabue viscosimeter
C—Inverted 100 cc. pipette
D—Steel ball viscosimeter
E—Stormer viscosimeter
  1—With 150 g. counterweight
  2—With 300 g. counterweight
  3—With 600 g. counterweight

For calibrating liquids, sugar solutions, glycerol, and castor oil of known viscosities were used. The most viscous liquid was castor oil at 10° C., with a viscosity of 2,400 centipoises. (A centipoise is 0.01 times the c. g. s. unit of viscosity. It is the viscosity of water at 20.2° C.) The absolute viscosities of the sugar solutions used were taken from the values given by Bingham and Jackson.[3] The glycerol used for standardization was J. T. Baker's C. P. product, diluted with water to a specific gravity of 1.2465 at 20° C., since this was the gravity of the most concentrated solution for which absolute viscosity values were available. Archbutt and Deeley's[4] values for the viscosities of glycerol solutions at 20° C. were adopted. Castor oil appears to be the most reliable calibrating liquid with a viscosity immediately above

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[1] Published by permission of E. I. du Pont de Nemours & Company.

[2] Presented at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

[3] Bureau of Standards, *Scientific Paper* **298**, 83.

[4] Bureau of Standards, *Technologic Paper* **112**, 23.

TABLE I

No.	LIQUID	Temp. ° C.	Specific Gravity	Kinematic Viscosity	Viscosity Centipoises	100 Cc. Pipette Discharge of 100 Cc. Sec.	Tagliabue Discharge of 70 Cc. Sec.	Inverted 100 Cc. Pipette Discharge of 100 Cc. Sec.	Steel Ball 10-in. Drop of Ball Sec.	Stormer 150 g. 100 Rev. Sec.	Stormer 300 g. 100 Rev. Sec.	Stormer 600 g. 100 Rev. Sec.
1	Water	20	0.9982	1.0	1.0	19.5	....	...	...	4.9	...	..
2	Sugar (59.9%)	40	1.2756	16.6	21.2	32.8	38.3	...	...	10.0	...	..
3	Sugar (59.9%)	30	1.2808	26.3	33.7	40.5	....	...	...	12.7	...	..
4	Sugar (59.9%)	20	1.2859	43.7	56.2	57.1	61.4	...	...	17.4	...	..
5	Sugar (59.9%)	10	1.2906	84.8	109.4	94.0	105.5	27.5	...	28.7	14.9	..
6	Glycerol	20	1.2465	385	480	410	444	117	...	109.7	52.9	26.5
7	Castor Oil	20	0.9570	1027	986	1106	1220	322	2.4	222	112.9	..
8	Castor Oil	10	0.9622	2500	2418	....	....	665	4.9	525	262.0	..

TABLE II

LIQUID No.	$\frac{V}{d}$ (Standard) Centipoises	100 Cc. Pipette: At (0.95t)	100 Cc. Pipette: $\frac{B}{t}$ Kinetic Correction $\left(\frac{490}{t}\right)$	100 Cc. Pipette: $\frac{V}{d}$ (Found) Centipoises	Tagliabue: At (0.87t)	Tagliabue: $\frac{B}{t}$ Kinetic Correction $\left(\frac{640}{t}\right)$	Tagliabue: $\frac{V}{d}$ (Found) Centipoises	Inverted 100 Cc. Pipette: At (3.3t)	Inverted 100 Cc. Pipette: $\frac{B}{t}$ Kinetic Correction $\left(\frac{170}{t}\right)$	Inverted 100 Cc. Pipette: $\frac{V}{d}$ (Found) Centipoises
2	16.6	31.2	14.9	16.3	33.3	16.7	16.6	..	.	..
3	26.3	38.5	12.1	26.4	..	..	..	..	.	..
4	43.7	54.2	8.6	45.6	53.4	10.4	43.0	..	.	..
5	84.8	89.3	5.2	84.1	91.8	6.1	85.7	90.7	6.2	84.5
6	385	389	1.2	388	386	1.4	385	386	1.5	384
7	1027	1051	0.4	1051	1061	0.5	1060	1062	0.5	1061
8	2500	..	..	..	..	..	..	2190	0.3	2190

V = Viscosity of the calibrating liquid as obtained from standard tables.
d = Observed density of the liquid.
t = Observed time (seconds) of outflow.

A and B are determined graphically from the curve obtained by plotting $\frac{V}{dt}$ against $\frac{1}{t^2}$.

that of glycerol, but there is considerable variation in different grades. The viscosity of the castor oil used in this work was taken from the values of Kahlbaum and Raber.[1]

The general form of equation calculating viscosity when an outflow viscosimeter is used is

$$\frac{V}{d} = At - \frac{B}{t} \qquad (1)$$

where V = viscosity in centipoises, d = density, t = time of discharge in seconds, and A and B are constants depending on the instrument. By the method of W. F. Higgins[2] we have derived values of A and B for the various outflow instruments. This method is based on the fact that when Equation 1 is divided by t the resulting equation is that of a straight line with values of $\frac{V}{dt}$ as ordinates and $\frac{1}{t^2}$ as abscissas. A is the intercept on the axis of $\frac{V}{td}$ and B is the slope of the line. The values of V, d, and t are known and the curve can therefore be plotted and A and B determined from it. Table I gives the experimental data from which curves were plotted and equations derived for the various instruments.

(A) 100 CC. PIPETTE—This was the ordinary 100 cc. pipette contained in a glass water jacket. The reading recorded was the time of outflow (in seconds) of 100 cc. of solution between two graduations about 2 in. above and 2 in. below the bulb. When used with a solution, the time of discharge of which was 400 sec., it began to drip after about 50 cc. had run out, indicating that its use with pyroxylin solutions of equal viscosity containing volatile solvents would introduce inaccuracy. For solutions of lower viscosity the 100 cc. pipette gave closely checking readings.

Evaluating the constants A and B in Equation 1 as indicated in Fig. 1, we find the equation for this particular 100 cc. pipette to be

$$\frac{V}{d} = 0.95t - \frac{490}{t}. \qquad (2)$$

(B) TAGLIABUE VISCOSIMETER—The Tagliabue viscosimeter was filled to the mark "90," which corresponds to a volume of 90 cc., and capillary tip "70" was used. The reading was the time in seconds of discharge of 70 cc. of solution.

As shown in Table II the variation between actual and calculated values of $\frac{V}{d}$ is very small, being of the same order as that found for the 100-cc. pipette. This instrument covers practically the same range of viscosities as the 100-cc. pipette and possesses the same degree of accuracy. However, since the capillary tip is more difficult to clean and the temperature regulation and manipulation in general are more complicated, we prefer the 100-cc. pipette for low viscosity work. The equation is

$$\frac{V}{d} = 0.87t - \frac{640}{t}. \qquad (3)$$

(C) INVERTED 100-CC. PIPETTE—The 100-cc. pipette already referred to was inverted and the solution allowed to flow through the discharge tube which had no constriction at the tip. The pipette was water-jacketed in the regular manner. The equation used for calculating $\frac{V}{d}$ with this particular instrument was found to be

$$\frac{V}{d} = 3.3t - \frac{170}{t}. \qquad (4)$$

Concordant results are difficult to obtain with this instrument and it has been our experience that when high viscosity pyroxylin solutions containing volatile solvents are used it is practically impossible to obtain closely agreeing readings. This is indicated in Table II by the large variation between actual and calculated viscosities of liquid No. 8.

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[1] Bureau of Standards, *Technologic Paper* **112**, 24.

[2] *J. Soc. Chem. Ind.*, **32** (1913), 568.

In the case of the Stormer and steel ball viscosimeters the type of equation applicable to the outflow instruments does not apply. In the outflow type the head of liquid furnishes the only source of energy used to overcome viscous resistance; in the Stormer instrument the energy is supplied by an external force independent of head.

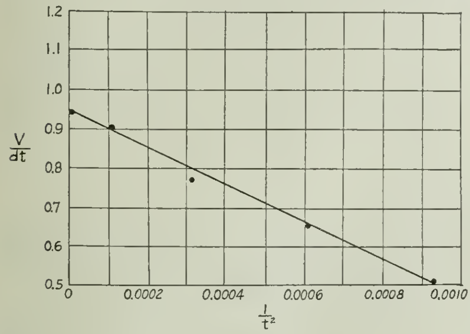

Fig. 1—Graphical Derivation of Constants A and B in Equation 1 by Method of W. F. Higgins

V = viscosity (centipoises); d = specific gravity; t = observed time of outflow (seconds)

(D) STEEL BALL VISCOSIMETER—A polished steel ball (diameter 0.250 in., weight 1.045 g.) was dropped through a hole in a stopper at the top of a vertical tube of 1.375 in. inside diameter. The reading was the time which it required to fall between two marks 10 in. apart. The tube was 13 in. long and the space below the bottom mark was 1.75 in.

S. E. Sheppard[1] has found that for high viscosity solutions the simple mathematical relation between viscosity and time of fall given by Stoke's law holds sufficiently close for industrial purposes, provided the ratio of diameters of the tube to the ball is at least 10; for smaller ratios he applies a correction.

In our standardization the greatest time observed was 4.9 sec., obtained with castor oil at 10° C. It is difficult, therefore, to standardize the instrument accurately since calibrating liquids of higher viscosity are not readily available. We had considerable difficulty in obtaining concordant results on the same pyroxylin solution because of the uncertainty of the temperature throughout the viscous mass.

(E) STORMER VISCOSIMETER—The Stormer viscosimeter and its applications have been discussed by Rodgers and Sabin[2] and by Rigg and Carpenter.[3]

In our experiments the inverted hollow cylinder was inserted in 85 cc. of the solution which was contained in the cup. The rotating cylinder was lowered to a definite point for each determination; the observed reading was the time of 100 revolutions.

Unlike the outflow viscosimeters, which can give only kinematic viscosity directly, the Stormer readings are unaffected by the density of the solution and give absolute viscosity. Plotting absolute viscosities as ordinates against time of 100 revolutions as abscissas (see Fig. 2) the points are found to lie along a straight line. The equation is therefore of the type $V = At + B$, where B is the value of V when $t = 0$ and $A = \frac{V - B}{t}$ at any point on the line. From Fig 2 we find that when $t = 0$, $V = -25 = B$. Taking this value of B(—25) and substituting in the equation $A = \frac{V - B}{t}$ at any point of the curve, we find $A = 4.6$. The equation for calculating absolute viscosity from the observed reading of this instrument when the 150 g. counterweight is used is therefore

$$V = 4.6t - 25. \qquad (5)$$

TABLE III

Liquid	Actual Viscosity Centipoises	Stormer Viscosimeter: 150 G. Counterweight Calc. $V = 4.6t - 25$	Stormer Viscosimeter: 300 G. Counterweight Calc. $V = 9.3t - 30$
Sugar Solution (59.9%)	21	21	..
Sugar Solution (59.9%)	33	33	..
Sugar Solution (59.9%)	56	55	..
Sugar Solution (59.9%)	109	107	108
Glycerol	480	481	462
Castor Oil	986	996	1020
Castor Oil	2418	2390	2407

For high viscosities it is desirable to have a lower reading. With this in view a 300 g. counterweight was tried, with the result that the time of 100 revolutions was almost exactly halved. For viscosities of at least 500 centipoises it can be used to advantage.

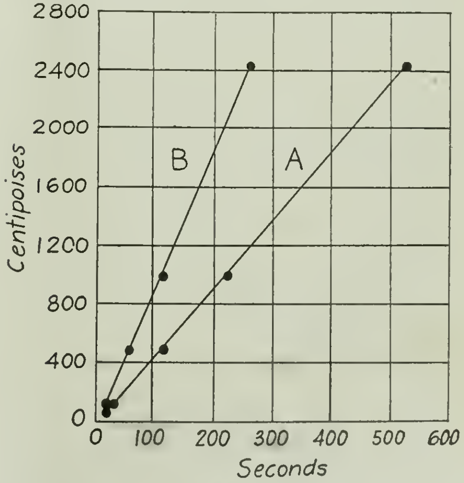

Fig. 2—Stormer Viscosimeter

Relation of viscosity (centipoises) to time of 100 revolutions (seconds) of inverted cup. Curve A shows relation when 150 g. counterweight is used; Curve B, when 300 g. counterweight is used

By calculations similar to the above we find the equation of the Stormer instrument when using a 300 g. counterweight to be

$$V = 9.3t - 30. \qquad (6)$$

A 600 g. counterweight gave a reading of 26.5 sec. on solution which gave a reading of 52.9 sec. with a 300 g. counterweight. Evidently the speed of revolution of the cylinder varies directly with the magnitude of the counterweight. Since all the points lie so nearly on a straight line there is no reason to doubt that Equations 5 and 6 can be used for viscosities higher than those observed.

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[1] This Journal, **9** (1917), 523.

[2] *Ibid.*, **3** (1911), 737.

[3] *Ibid.*, **4** (1912), 901.

Equation 5 derived for the Stormer viscosimeter with 150 g. counterweight does not hold for very low viscosities. Table IV gives experimentally determined readings obtained with liquids of known low viscosities.

TABLE IV

LIQUID	Temp. ° C.	Time of 100 Rev. Sec.	Absolute Viscosity Centipoises	Calculated Viscosity ($V = 4.6t - 25$)
Acetone	20	3.9	0.33	..
Distilled water	50	4.5	0.55	..
Distilled water	20	4.9	1.00	..
Sugar (19.90%)	30	5.4	1.50	0.38
Sugar (19.90%)	20	5.6	1.96	0.76
Sugar (38.85%)	40	6.1	3.23	3.9
Sugar (38.85%)	20	6.9	6.17	6.7
Sugar (38.85%)	15	7.3	7.43	8.6
Sugar (59.90%)	50	8.6	15.0	14.5

Fig. 3 should be used for viscosities up to 15 centipoises, above which the equation is sufficiently accurate.

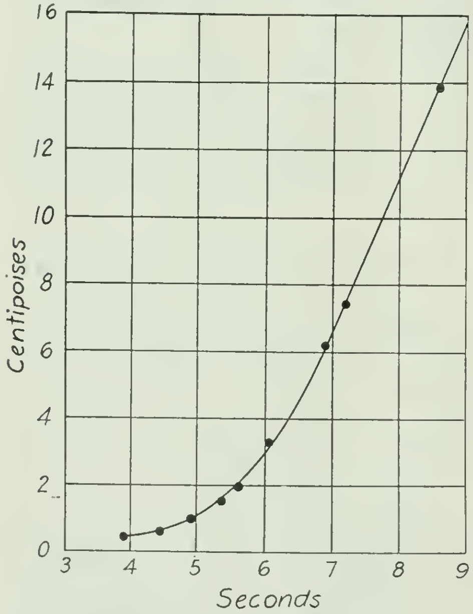

FIG. 3—STORMER VISCOSIMETER

Relation of viscosity (centipoises) to time of 100 revolutions (seconds) of inverted cup at low viscosities. This curve is for the Stormer viscosimeter with a 150 g. counterweight at viscosities at which the relation is no longer linear

INSTRUMENT CORRECTION

It is erroneous to assume, as is commonly done, that viscosity is proportional to time of outflow, because, as it has frequently been pointed out:

(*a*) Part of the energy is expended in setting the liquid in motion and not in overcoming viscous resistance. The factor which takes this effect into account is known as the kinetic correction and may be of a magnitude as great as viscosity itself for very fluid solutions. Furthermore, this correction is a variable.

(*b*) Even at a viscosity so high that the kinetic correction is negligible, the time of discharge of an outflow viscosimeter is a measure of kinematic viscosity only (*i. e.*, absolute viscosity divided by specific gravity) and not of absolute viscosity. Hence, unless densities are equal, readings are not strictly proportional to viscosities.

The instrument correction for outflow viscosimeters corresponds to the kinetic correction (B/t), while for the Stormer viscosimeter it represents the friction factor of the instrument. The correction values for the various instruments at the viscosities of the standard calibrating liquids are shown in Table V.

TABLE V

		——INSTRUMENT CORRECTION (Ceotipoises)——			STORMER —VISCOSIMETER—	
Viscosity Centipoises	$\frac{\text{Viscosity}}{\text{Density}}$	100 Cc. Pipette	Tagliabue	Inverted 100 Cc. Pipette	150 G. Counter-weight	300 G. Counter-weight
21.2	16.6	—14.6	—16.7	...	—25	..
33.7	26.3	—12.2	...	...	—25	..
56.2	43.7	—10.5	—9.7	...	—24	..
109.4	84.8	—4.5	—7.0	—5.9	—23	—29
480	385	—4	—1	—1	—26	—12
986	1027	—24	—34	—35	—35	—64
2418	2500	..	..	+310	+3	—19

It will be observed from Table V that the instrument correction for the Stormer viscosimeter with 150 g. counterweight is practically constant over a viscosity range of 20 to 500 centipoises, above which the 100 cc. pipette and Tagliabue viscosimeter begin to drip and are therefore undesirable for use with pyroxylin solutions. The Stormer instrument thus possesses a decided advantage over these outflow viscosimeters. Although the correction shows considerable variation at the two highest viscosities indicated in Table V, it must be remembered that these points refer to castor oil, the viscosity of which is somewhat uncertain. At viscosities over 500 centipoises, however, the constant correction may be neglected for most practical work.

CONCLUSIONS

1—Outflow viscosimeters with small orifices are suitable for use with solutions of low viscosity, provided that the kinetic correction and the specific gravity are considered.

2—The steel ball viscosimeter is unsuitable for use except with solutions of very high viscosity and hence is not universally applicable to pyroxylin solutions. It is unreliable because of the difficulty of obtaining a uniform temperature throughout the viscous solution in the large tube, in which it is difficult to stir the solution without the formation of air bubbles.

3—The Stormer viscosimeter has apparently the greatest range of all those examined. It has given closely checking results with solutions varying in viscosity from about ten times that of water to 200 times that of castor oil at 20° C. The temperature is under control and is easily maintained constant once the desired point is reached, since the solution is not removed from the container during the operation. By covering the container, loss of volatile solvent through evaporation is reduced to a minimum. Manipulation is easy and determinations can be made more rapidly than with any of the other types investigated. It has the further advantage over outflow instruments of giving true instead of kinematic viscosity.

4—In conclusion we wish to emphasize the importance of expressing viscosities in absolute units. The additional time required is slight and its expenditure is well repaid; not only are all results made of permanent value and directly comparable, being entirely independent of the instrument employed, but any possible confusion between the manufacturer and the trade, which often arises due to the use of a multiplicity of empirical standards, is entirely avoided.

THE RAPID PREPARATION OF TABLES[1]

By J. C. Witt
Pittsburgh, Pennsylvania

Received January 2, 1920

In commercial and manufacturing control laboratories, certain determinations and tests are made a great many times, and the calculation of results becomes tiresome. To lessen this work, various types of computing apparatus, charts, and factor tables are employed. The desirability and usefulness of a table are often recognized long before a chemist has the time to prepare one or can bring himself to begin the considerable amount of uninteresting work necessary. Logarithm tables or some type of slide rule may be used. The former, however, requires considerable time, and the latter is often insufficiently accurate for chemical calculations.

Table I

	d_A ↓ b_1 2.332	d_B ↓ b_2 2.478	d_C ↓ b_3 2.624	d_D ↓ b_4 2.770	d_E ↓ b_5 2.916	0
$d_1 \longrightarrow \overset{c_1}{0.5102}$	a	$a + d_1$	$a + 2d_1$	$a + 3d_1$	$a + 4d_1$	1
$d_2 \longrightarrow \overset{c_2}{0.5175}$	$a + d_A$	....	....	....	....	2
$d_3 \longrightarrow \overset{c_3}{0.5248}$	$a + 2d_A$	....	....	....	....	3
$d_4 \longrightarrow \overset{c_4}{0.5321}$	$a + 3d_A$	....	....	....	....	4
$d_6 \longrightarrow \overset{c_6}{0.5394}$	$a + 4d_A$	....	....	....	....	5
$d_6 \longrightarrow \overset{c_8}{0.5467}$	$a + 5d_A$	....	....	....	....	6
$d_7 \longrightarrow \overset{c_7}{0.5540}$	$a + 6d_A$	....	....	....	....	7
$d_8 \longrightarrow \overset{c_8}{0.5613}$	$a + 7d_A$	....	....	....	....	8
$d_9 \longrightarrow \overset{c_8}{0.5686}$	$a + 8d_A$	....	....	....	....	9
$d_{10} \longrightarrow \overset{c_{10}}{0.5759}$	$a + 9d_A$	....	....	....	....	10
	A	B	C	D	E	

$b_1 = 2\ 332$

$c_1 = 0.5102$

$a = b_1c_1 = 1.18979$

$d_I = \frac{b_5 - b_1}{5 - 1} = 0.146$ (for index line)

$d_{II} = \frac{c_{10} - c_1}{10 - 1} = 0.0073$ (for index columu)

$d_{III} = d_Id_{II} = 0.00107$

$d_A = b_1d_{II} = 0.01702$

$d_1 = c_1d_I = 0.07449$

In preparing the ordinary type of table the quantities involved can usually be so manipulated that the principal labor consists in multiplying one series of numbers by another number or series of numbers. Also it very frequently happens that one or both series are in the form of arithmetical progressions. When the numbers fulfill these conditions, the table may be prepared with little labor. There is nothing new about the principles involved, but their application enables one to prepare a table, accurate to any desired number of decimal places, much more rapidly than by the use of logarithms, and to check easily the correctness of the results. The greater the number of terms, the more rapidly, relatively, a table can be prepared, because the preliminary work is independent of the size of the table.

To explain the procedure, we may refer to Table I which is similar to one the writer recently had occasion to prepare. Suppose it is desired to multiply 2.332, 2.478, 2.624, 2.770, and 2.916, respectively, by 0.5102, 0.5175, 0.5248, 0.5321, 0.5394, 0.5467, 0.5540, 0.5613, 0.5686, and 0.5759, respectively, carrying out the results to the fourth decimal place. Designate the first series by b_1, b_2, ... b_5, and the second series by c_1, c_2, ... c_{10}. Draw the outline of the table and set down the numbers in the index line and in the index column. The index line is a progression, of which the common difference, d_I, is $\frac{2.916-2.332}{5-1} = 0.146$; and the index column is a progression, of which the common difference, d_{II}, is $\frac{0.5759-0.5102}{10-1} = 0.0073$. Let the first, or least, term of the table be a. We shall discuss two cases; (1) when only one series is in progression, and (2) when both series are in progression.

ONE SERIES IN PROGRESSION—Let us consider that the index column of Table I is in progression but that the index line is not. The terms of line 1 are calculated by performing the indicated multiplication and carrying the results out to at least one more decimal place than is required in the finished table.[1]

Now each column of the table will be a progression, of which the first term is known. The common difference of each column is equal to the product of the index of that column and the common difference of the index column. For example $d_A = b_1d_{II}$, $d_B = b_2d_{II}$, etc. It may be seen that if the common difference of the index column is one, the common difference of each column will be the same as the index of that column. The remaining terms of each column may then be found by successively adding the common difference of the column to the first term. In case the index line of a table is in progression and the index column is not, the table may be prepared by first finding the terms in the first and last columns, and then computing the remaining terms by use of the common difference of each line.

The only systematic error which arises in substituting this method of calculation for multiplication is due to the fact that in many cases the exact common difference cannot be found, and there is an error in the last decimal place not to exceed ±5. When the extra decimal place is dropped at the completion of the table, in rare cases a term will differ from the value found by multiplication by ±1 in the last place. Since the last decimal place is usually not exactly correct even when the term has been found by multiplication, however, the true error due to the substitution of addition for multiplication is less than the apparent error. For example, suppose in calculating the terms for a 4-place table, a term is 0.45934 by multiplication, and 0.45935 by the short method. This will be set down in the first case as 0.4593 and in the second case as 0.4594—an apparent error of +1. However, the error in the first case is —0.00004 and in the second, +0.00005. Therefore, the true error caused by the short method is only 0.00001, which is negligible. The error may be made less than any given value by increasing the number of decimal places of the terms, during the process of preparing the table.

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[1] Copyrighted 1920 by J. C. Witt.

[1] During the process of preparing the table all the terms and common differences should be carried to at least one more decimal place than is required in the finished table. The extra place is dropped when the table is completed.

Any accidental error is easily found, except in the very unlikely case of compensation of errors. For example, in finding the terms of a given column, the last term as found by adding the common difference is compared with the same term as found by multiplication, and if the difference between the two results is greater than ±5 in the last decimal place, an accidental error exists some place in that column. It often saves time, to find all the terms of the last line by multiplication at the beginning so that the accuracy of each column may be checked as completed.

BOTH SERIES IN PROGRESSION—In this case, the method of preparation may be still further shortened. Aside from checking the accuracy of the results, it is necessary to prepare only one term, a, by multiplication. After performing two other multiplications, the remainder of the work may be done by addition alone. When both the index line and the index column are in progression, then every column and every line will be in progression. In finding the terms of the first line, a is the first term of the progression. The common difference is the product of the index of the line and the common difference of the index line, or, $d_1 = c_1d_\mathrm{I} = 0.5102 \times 0.146 = 0.07449$. By adding this quantity successively to a, all the terms of the first line may be found. As has been explained, the common differences for the columns are as follows:

$$d_\mathrm{A} = b_1d_\mathrm{II}d_\mathrm{B} = b_2d_\mathrm{II}, \text{ etc.}$$

But

$$b_2 = b_1 + d_\mathrm{I},\ b_3 = b_1 + 2\ d_\mathrm{I}, \text{ etc.}$$

Therefore, we may consider these common differences themselves as in progression (line 0). The first term is $b_1d_\mathrm{II} = 0.01702$. The common difference of the series is $d_\mathrm{I}d_\mathrm{II}$, or d_III. The series is therefore b_1d_II, $b_1d_\mathrm{II} + d_\mathrm{III}$, $b_1d_\mathrm{II} + 2\ d_\mathrm{III}$, etc. Now, having the first term and the common difference for each column, the table may be readily completed. The common differences for the lines are also in progression (column 0). The first term is c_1d_I and the common difference is d_III.

To check the results for accidental errors, a term may be calculated by multiplication or by adding a multiple of the common difference of that line to the first term in the line.

The systematic errors are likely to be greater than in the first case. There is an error due to the common difference of line 0, of line 1, and to the common difference of each column. Of course these will either combine or compensate each other, depending on the signs. In starting a table, especially a large one, it is well to check the last term in line 0, line 1, and Column E, to see how much the maximum error will be in each case. If it is greater than desired, the number of decimal places may be increased, or in the case of a table with 50 to 100 columns, the true values, line 0 and line 1, may be calculated by multiplication for every 5 or 10 columns and the remaining terms of those lines filled in by use of the common differences. After several tables have been prepared by this method, many ways of looking for accidental and regular errors will present themselves.

It is of interest, though of no practical importance, that any term, t, may be found by the following formula, in which n_1 is the number of the column in which the term is sought, diminished by one, and n_2 is the number of the line, diminished by one:

$$t = a + n_1c_1d_\mathrm{I} + n_2b_1d_\mathrm{II} + n_1n_2d_\mathrm{III}$$

In case the common difference of the index line and that of the index column are the same quantity, d, this formula will become

$$t = a + (n_1c_1 + n_2b_1)d + n_1n_2d^2.$$

The method of preparation may be further illustrated by Table II, where the numerical relations are so simple they may be seen at a glance. We shall consider only the second case, where both series are in progression. The index line is 4, 6, 8, 10, 12, and the index column is 2, 5, 8, 11, 14. It may be readily seen that the common difference of the index line is 2, the common difference of the index column is 3, and the first (and least) term of the table is 8. Now the common difference of line 1 is equal to the index of that line times the common difference of the index line, or 2 × 2 = 4. Starting with 8, we add 4 successively, obtaining 8, 12, 16, 20, 24 for the terms of line 1. In the same way the common difference of Column A is 4 × 3 = 12. By adding successively the product of the common difference of the index line and that of the index column (2 × 3 = 6) we obtain 12, 18, 24, 30, and 36 as the common differences of Columns A, B, C, D, and E, respectively. Now having the first term and the common difference of each column, the other terms of each column may be rapidly found.

TABLE II

Index column						
	$\longrightarrow$ 4 × 3 = 12	12 + 6 = 18	18 + 6 = 24	24 + 6 = 30	30 + 6 = 36	
	Index Line 4	6	8	10	12	Line
	$\longrightarrow$	8 + 4 =	12 + 4 =	16 + 4 =	20 + 4 =	
2	↓ 8	↓ 12	↓ 16	↓ 20	↓ 24	1
5	8 + 12 = 20	30	40	50	60	2
8	20 + 12 = 32	48	64	80	96	3
11	32 + 12 = 44	66	88	110	132	4
14	44 + 12 = 56	84	112	140	168	5
Column	A	B	C	D	E	

SOME NOTES ON THE BAUMÉ HYDROMETER

By George H. Taber
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Received December 10, 1919

After the name crude oil and the names of some of its products, the first thing likely to come to the attention of anybody engaging in the petroleum business, or studying it theoretically or practically, is a reference to what is called the "Baumé gravity" of the oils; but it is a conservative assertion that a very large majority of the users of the Baumé hydrometer and its readings are under some one or more misapprehensions in regard to the instrument, its principles or their application. It is quite likely, as some readers may point out, that the present writer shares in some of these misapprehensions, but, if so, they are self-inflicted and of long standing.

Baumé hydrometers are of the constant-weight, variable-volume type. As an aid to understanding what the Baumé instrument is, and what it is not, it will be well first to consider the constant-weight, variable-volume specific gravity hydrometer, which it is precisely like except in its stem divisions and numbers.

The basic principle of all hydrometers is that a floating body displaces an amount of liquid equal to its own weight. As the weight of the hydrometer under consideration is constant, the same weight of all liquids is displaced by it when floating freely in them, and the specific gravities of the liquids vary inversely as the volumes displaced, these volumes being indicated by marks on the stem of the hydrometer, accompanied by numbers giving the corresponding specific gravities.

Since the numbers marked on the stem delimit equal increments of specific gravity, and the volumes immersed vary as the reciprocals of these numbers, the successive volumes will necessarily form a harmonic series, the differences between the successive terms of which will increase as the specific gravities decrease; that is, the spaces between the divisions showing equal increments of specific gravity increase in width from the bottom to the top of the stem. The same thing may be stated in another way: namely, if the successive specific gravities marked on the stem be considered as abscissas of a rectangular hyperbola, the constant k of whose equation equals the volume immersed when the hydrometer is floating in water, the successive total volumes immersed will correspond to the ordinates of the hyperbola.

It will be seen from the preceding paragraph that if, reversing the usual practice, the stem of the specific gravity hydrometer were graduated with equispaced divisions to show the volume immersed, the corresponding specific gravities would not decrease by equal decrements, but these decrements would decrease in amount from the bottom to the top of the stem.

Disregarding the principles upon which the graduation and markings of the stems of Baumé hydrometers were originally based, and the object of their adoption, and without going into details as to the differences in scales which have prevailed in the past—some of which still persist—it suffices to state here that Baumé scales are now based on mathematical formulas, and that the formula which has the most authority in this country for liquids heavier than water is

$$\text{Bé.}^{\circ}_{\text{H}} = 145 - \frac{145}{\text{Sp. Gr.}_{60^{\circ}/60^{\circ}}}, \text{ or}$$

$$\text{Sp. Gr.}_{60^{\circ}/60^{\circ}} = \frac{145}{145 - \text{Bé.}^{\circ}_{\text{H}}};$$

and for liquids lighter than water—

$$\text{Bé.}^{\circ}_{\text{L}} = \frac{140}{\text{Sp. Gr.}_{60^{\circ}/60^{\circ}}} - 130, \text{ or}$$

$$\text{Sp. Gr.}_{60^{\circ}/60^{\circ}} = \frac{140}{130 + \text{Bé.}^{\circ}_{\text{L}}},$$

145 being what is called the modulus of the former scale, and 140 that of the latter.

Examining the formula for liquids heavier than water, we see that $\text{Bé.}^{\circ}_{\text{H}}$ = *the reciprocal of the specific gravity* multiplied by 145, and the product subtracted from 145; and that the greater the specific gravity, the greater the equivalent Bé._{H} degrees. From the formula for liquids lighter than water, we see that $\text{Bé.}^{\circ}_{\text{L}}$ = *the reciprocal of the specific gravity* multiplied by 140, and the product diminished by 140 less 10; and that the greater the specific gravity, the smaller the equivalent Bé._{L} degrees. The deduction of 10 from the modulus, which is in effect deducting the modulus and adding 10 to the result, shows that water is 10° by this scale, instead of 0° as by the heavy scale.

Since, as previously stated, the specific gravity varies inversely as the volume of liquid displaced, if the stem of a specific gravity hydrometer were divided to show equal increments of immersion, the corresponding specific gravity numbers would form a harmonic series; and since the equivalent Baumé degree numbers are reciprocals of a harmonic series of specific gravities, modified only by being multiplied by a constant and added to another constant, they form an arithmetic progression, and if these Baumé degree numbers were applied to such a scale, we should have an equispaced scale with equicrescent numbers, or in fact a Baumé scale,—heavy or light according to the conversion formula used.

The following are some frequently misunderstood points:

1—The name is Baumé, not Beaumé.

2—Specific gravity numbers are ratios, not degrees. Baumé numbers are degrees, not ratios.

3—The Baumé scale is not inaccurate, and it is not unscientific. From its equispaced divisions, it is likely to be more correctly divided in the making, the correctness of its graduations can be more easily checked, and almost anyone can interpolate its markings readily by the eye, whereas correct, rapid interpolation between specific gravity graduations is practically impossible. Of course, in significance, Baumé degrees are inferior to specific gravity ratios, and it requires one more step in calculation to convert them into pounds per gallon or other absolute density standards; however, the Baumé scale has become so fastened to the petroleum business that in all probability the world's supply of crude oil would be exhausted before it could be pried loose.

4—As is well known, the specific gravity of a mixture of equal volumes of two liquids when there is no contraction or expansion of volume from mixing, will be the arithmetic mean of that of each of the two constituents. If the reason for this is not obvious, change the specific gravities of the constituents to pounds per gallon by multiplying each by the number of pounds in a gallon of water at 60° F. Say the results are, respectively, 6 and 8 lbs. per gallon. It is obvious that if 1 gallon weighing 6 lbs. be mixed with 1 gallon weighing 8 lbs., the result will be 2 gallons weighing 14 lbs., 1 gallon of which mixture will weigh 7 lbs., 7 being the arithmetic mean of 6 and 8; and dividing 7 by the number of pounds in a gallon of water, we shall get the specific gravity of the mixture, which it will be seen must be the arithmetic mean of the specific gravities of the two constituents. By an extension of this reasoning it will be seen that the specific gravity of a mixture of any number of constituents in any proportions can be calculated in the same way; in other words, all problems of alligation medial and alligation alternate relating to liquids can be calculated directly by their volumes and specific gravities when there is no contraction or expansion of volume resulting from the mixing.

Contrary, however, to a somewhat generally held opinion, such computations cannot be made by direct use of Baumé degrees of either the light or heavy scale, although when the densities of the liquids are fairly close together the error may not be prohibitive, but the further apart the constituents are in density, the greater the error. Let us test the simplest case as follows:

Consider that we have equal volumes of two liquids of, respectively, a° Bé.$_L$ and b° Bé.$_L$. Take the arithmetic mean of the Baumé degrees of the two constituents, convert this mean into specific gravity and equate it to the arithmetic mean of the equivalent specific gravities of the two constituents; solve the equation, and ascertain the relation necessary between a and b to make the equation possible.

We have

$$\frac{140}{130+\frac{a+b}{2}} = \frac{\frac{140}{130+a}+\frac{140}{130+b}}{2}$$

which after expansion and reduction results in

$$a^2 - 2\,ab + b^2 = 0$$
$$a - b = 0$$
$$a = b$$

or in words, the only case in which the degrees Baumé of a mixture of equal volumes of two liquids lighter than water are the arithmetic mean of the degrees Baumé of the constituents, is when both are the same. The same result ($a = b$) would have been obtained if we had taken a° Bé.$_H$ and b° Bé.$_H$ and made the conversions by the formula for the heavy scale. Consequently, in order to calculate the Baumé degrees of a mixture, it is necessary to convert the Baumé degrees of the constituents into specific gravities (or weights per volume, like lbs. per gallon), make the calculation on these, and convert the result by the formula into the corresponding Baumé degrees.

As a concrete arithmetic example is more convincing to some, and to give an idea of the possible error in averaging Baumé degrees, consider a mixture of equal volumes of liquids of 10° Bé.$_L$ and 70° Bé.$_L$. Averaging them by the Baumé degrees (which we have just proved an incorrect method), we should get 40° Bé.$_L$ for the mixture. Averaging them by their equivalent specific gravities 1.000 and 0.700 (the correct way), we get 0.850 specific gravity, equal to 34.7° Bé.$_L$.

However, if *weights* are used instead of *volumes*, problems in alligation relating to liquids can be performed directly with Baumé degrees of either the heavy or light scale, as seen from the following considerations, while they cannot be performed directly with specific gravities. Take the simplest case,—say equal *weights* of two liquids, respectively, 0° Bé.$_H$ and 95° Bé.$_H$. The arithmetic mean of the two is 47.5° Bé.$_H$. The specific gravities of the two constituents are, respectively, 1.000 and 2.900. As their weights are equal, the volumes may be taken, respectively, as 29 and 10. 29 vols. of 1.000 sp. gr. and 10 vols. of 2.900 sp. gr. average $1.487\frac{7}{59}$ sp. gr. = exactly 47.5° Bé.$_H$, which proves the contention in this simple case. By a laborious calculation, it can be demonstrated perhaps more conclusively. Take a lbs. of l° Bé., b lbs. of m° Bé., c lbs. of n° Bé. First, multiply each number of Baumé degrees by the number of lbs.; divide the sum of the products by the sum of the lbs., and the quotient will be the Baumé degrees of the mixture. Second, convert the Baumé degrees of each component into specific gravity. By use of the respective specific gravities, convert each number of pounds into gallons, perform the alligation in the usual way, and convert the resulting specific gravity into Baumé degrees, when the result will be seen to be the same as that of the first operation where the Baumé degrees were used directly.

From the foregoing it will be seen that while *specific gravities* and *weights per unit of volume* are closely related to each other (in the metric system they are practically the same), *Baumé degrees, light or heavy,* are related, although more remotely, to *volumes per unit of weight.* This fact and the deduction from it that alligation problems dealing with the *weights* of the component and resultant liquids can be worked directly with Baumé degrees, may be well known, but the writer has never heard or seen them referred to orally or in print.

5—Frequently a would-be purist in nomenclature, who approaches the oil business from a scientific viewpoint, condemns the oil man for using the expression "Baumé gravity," and tries to persuade him to say "Baumé specific gravity," which is more cumbersome and further from being correct. If time in speaking and time and space in writing were of no importance, we might be absolutely precise and say, for instance in using the light Baumé scale: "The oil is of a specific gravity equivalent to 50 degrees Baumé." However, this is entirely unnecessary, and the expression, "The oil is 50 Baumé gravity," cannot be misunderstood and is entirely justifiable. In speaking of the "degrees gravity" of an oil, the refiner follows the practice of the brewer who speaks of the "degrees of gravity in a wort," but happily for the brewer his gravity degrees are much more easily converted into specific gravities than those of the refiner.

One meaning of the word gravity is "weight." Some refiners speak of "weighing" an oil, where most, meaning the same thing, call it "taking the gravity." The word gravity has done duty since the early days for both specific gravities and for Baumé degrees, and its use in this way is convenient. When the figures are attached there is little chance of misunderstanding which one is meant; but in the case of oil, the common expressions "higher gravity" and "lower gravity" have directly opposite meanings, depending upon whether the specific gravity or light Baumé gravity is referred to. The first time this came to the writer's attention was when some thirty-seven years ago he heard two oil manufacturers spend much of an afternoon talking at cross purposes, because when one spoke of a certain equipment's giving a higher or lower gravity in the product, the speaker had in mind specific gravity, while the other, who was unable to agree with the views expressed, understood Baumé gravity to be meant. The writer then determined that to afford himself the convenience of using the word gravity without being misunderstood, he would say in making comparisons, "*heavier*" or "*lighter* gravity," which would convey the same meaning whether applied to specific gravity or to Baumé degrees, and he has been trying ever since to persuade others to use in such cases the words "heavier" and "lighter" instead of "higher" and "lower," or "lower" and "higher," but with more or less lack of success.

A reprehensible expression often used in oil contracts is "The oil shall be (say) 30° gravity or *better*." The meaning of the word "better" is obscure, as it depends on the opinion of the customer or a knowledge of the use to which the oil is to be put, to decide whether it would be better if it were heavier, or better if it were lighter.

To return to the subject in the beginning of this subhead, it is probable that if our theoretic friends wish to do away with the use in the oil business of the convenient and time-honored word "gravity" as applied both to specific gravities and Baumé degrees, and the convenient and time-honored combination "Baumé gravity" as applied to the latter, they will have to first kill off all the old-timers and then at least the second and third generations.

A MODIFIED FORM OF THE SMITH FERMENTATION TUBE

By Aubrey Vail Fuller

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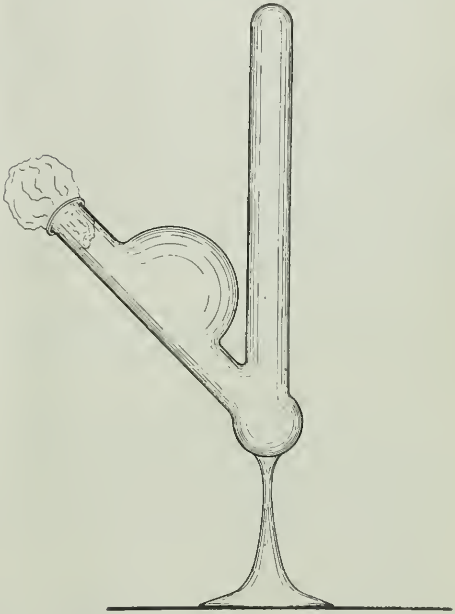
Received February 16, 1920

It is frequently the case, especially in dealing with commercial problems, that the analyst desires early information as to the presence of organisms capable of causing the active fermentation of certain sugars. To this end it is the practice to inoculate a fermentation tube, of either the Smith or Durham type, with a portion of the sample under examination, incubate and await developments. While, of course, this method yields satisfactory results when proper precautions regarding inoculation and incubation are observed, it is believed that, for rapidity and certainty, the modified construction of the tube pictured here offers certain advantages over the forms commonly used.



The bulb, instead of being symmetrical, is made trough shaped on its under side in order to facilitate the falling of the growth to the lowermost portion of the gas tube proper, with the results that as the gas is liberated it rises vertically and is trapped without an occurrence of appreciable loss through the bulb, as is the case when the Smith type is used.

A very small quantity of fairly coarse acid-washed sand introduced into the depression aids materially in the disengagement of the gas as it is formed.

It has been found that within a given time the volume of gas collected in a tube of this type is about three times as great as is the case when the Smith type is used, the inoculum being the same both qualitatively and quantitatively.

From this fact it follows that this form of tube presents the additional advantages of enabling the bacteriologist to secure evidence more quickly as to the identity of the organism concerned by the customary "analysis" of the gas formed by the soda absorption method; and, further, that the results so obtained will be more accurate for a given period of incubation.

THE LABORATORY HOOD

By J. C. Witt

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Received January 10, 1920

Though the hood is an important part of the equipment of the chemical laboratory, its design often receives surprisingly little consideration. A number of excellent hoods may be found, but really satisfactory ones are comparatively rare, and for every even fair hood there may be found several that are decidedly faulty. Why this should be is difficult to explain. It may be partly due to the fact that the subject has not received much general discussion and little has been published concerning it.[1] The inconvenience that may be caused by a faulty hood, and the factors which make one good or bad are known to everyone with laboratory experience, yet it often happens that in installing a laboratory the chemist does not give the matter the thought it deserves, or from motives of economy does not spend the amount necessary for satisfactory construction. Then, too, many laboratories are installed in rooms not built for the purpose and the space available and the general arrangement are not favorable.

The design will depend to some extent upon the character and amount of work carried on in the laboratory for which it is built, but the essential points are as follows:

SIZE—The hood should be sufficiently large so that in case a hot plate is used, the walls will not be so close to the source of heat that the glass will be broken, the woodwork burned or the paint on the interior blistered. The hood should also be large enough to accommodate the work for which it is intended, but no larger than is necessary, as its efficiency may be considerably affected by the size.

FLOOR—The floor should be of some substance which is not readily affected by heat or by acids. Care should be taken to insulate the portion under the hot plate from the heat thrown down from the burners. One satisfactory way is to first place a heavy sheet of asbestos several inches longer and wider than the plate, then a sheet of iron sufficiently heavy to support all its load without bending. The iron plate is supported by small bricks or cement briquettes about one inch above the asbestos to provide an air chamber as a further insulator. White tiles are well adapted for use in most hoods. They are acid and heat resisting and assist in keeping the interior light. They are somewhat more expensive than most other materials used for the purpose, and considerable care must be taken in setting them, since otherwise shrinkage cracks, caused by heat inside the hood, are likely to appear.

LIGHT—When space permits the best location for a hood is in the center of a room, so that all the walls may be of glass. When this arrangement is not possible, the walls should be painted or enameled white and sufficient electric lights should be placed in the ceiling, or on the side walls high enough to be out of the direct line of vision, to keep the place well lighted. Even when the walls of the hood are of glass the electric lights should not be omitted because they are needed at night and on cloudy days. Since white paint will gradually grow yellowish or brownish from the effect of fumes, the walls should be repainted frequently. The paint should be inspected from time to time to see that it is not blistering or scaling off.

METAL INSIDE THE HOOD—As far as possible, metal inside the hood—especially iron or steel—should be avoided. It is not necessary to have any exposed metal above the level of the hot plate. Porcelain electric light fixtures may be used, and it is often possible to place these above the hood, allowing the light to pass through the glass roof. No matter how iron is plated or painted at the start, the metal is likely to be exposed in time to the action of fumes, after which it is not long before rust is dropping into vessels on the hot plate.

OUTLET PIPE—This should be made of tile or earthenware or possibly of lead, but never of iron. It is preferable for the pipe to leave the hood in a horizontal position rather than vertical, to lessen the chance of dust and dirt falling into the hood. If the pipe is vertical the lower end should be protected by a glass baffle plate. For the ordinary sized hood, having natural draft, the outlet pipe should be at least 8 or 10 in. in diameter, and there should be as few turns as possible. Round bends are, of course, preferable to right angles. It is best to connect the outlet pipe with a high chimney or stack when possible. When this is not possible a special stack high enough to give a satisfactory draft should be erected.

FORCED DRAFT—When it is possible it is much more satisfactory to construct a hood with natural draft only, and if the hood itself and outlet pipe are properly made and proportioned, as a rule no forced draft is necessary. The gases will move more readily to the outlet pipe if the roof slants in that direction than if it is in a horizontal plane. When the hood will not draw sufficiently unaided, a gas jet inside the stack or the outlet pipe or some form of exhaust fan may be employed. The former is to be recommended when it is practicable. The fan has the disadvantage of the expense of operation, and deterioration due to corrosive fumes. In building, where there are a number of hoods, it is often necessary to depend entirely on forced draft, and it is customary to connect all the hoods with one large exhaust fan. In many cases such an arrangement is not satisfactory, since it is very likely that the draft cannot be kept equal in all the hoods even with a system of dampers. A pipe may become clogged or a leak develop and thereby cut off the draft from a number of hoods. It is better to have a small exhaust fan for each hood. Down-draft hoods are sometimes made. These are, of course, better adapted to heavy gases such as sulfur trioxide than the lighter gases, but are often not satisfactory.

GAS AND WATER CONNECTIONS—Valves controlling the gas and water supply should be placed in the front, below the level of the floor of the hood. Otherwise it is awkward to reach the valves and one is likely to upset apparatus and spoil determinations. There should be a small sink in the hood so that liquid giving off fumes may be emptied without removal from the hood. In case the hood is of considerable length, there should be a slightly sloping tile trough or gutter connecting with the sink. Fuming or corrosive liquids if accidentally spilled may be washed into this and thus removed.

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[1] *Chem.-Eng.*, **9**, 21; **12**, 183; *Chem.-Ztg.*, **35**, 254; *J. Am. Chem. Soc.*, **37** (1915), 1726.

WINDOWS—It is sometimes recommended that the windows be made small. This arrangement has advantages especially when heavy fumes are produced. However, it is a sacrifice of working space because the available capacity of the hood is thereby considerably lessened. If the draft is sufficient, it is better to have the windows take up the whole front of the hood. When there are two windows it is convenient to connect the weight chains at the middle of the top of each one and connect the windows directly with each other, with no fixed support between. In this way when all are up there is no support to interfere and more room is available for work. Another advantage is that one window may be pulled down and substances likely to spatter into the eyes placed behind the glass.

ADDRESSES AND CONTRIBUTED ARTICLES

SELENIUM AND TELLURIUM[1]

By Victor Lenher

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The elements, selenium and tellurium, are not so rare as is generally supposed. Indeed the term "rare element" is a rather vague and indefinite expression. Titanium, for example, is commonly regarded as such though F. W. Clarke has shown it to be more plentiful than carbon, sulfur, and phosphorus combined. Titanium is, therefore, very plentiful but the number of its chemical compounds is very limited.

A recent estimate of the amount of selenium and tellurium that can be produced in the United States, without making any material additions to the present plants, has shown that this country can furnish more than 300,000 pounds of selenium and about 125,000 pounds of tellurium annually. The elements are commonly marketed in elementary form although some of the refineries have produced small quantities of derivatives such as sodium selenite and tellurium dioxide.

USES FOR THESE ELEMENTS

The chemical characteristics of these two elements closely follow those of sulfur; indeed, the types of selenium and tellurium compounds are in general those of sulfur, but owing to their higher atomic weights they are more metallic. Tellurium in elementary form looks much like antimony. It is white and so strongly crystalline that it is quite brittle and can be easily powdered. Toward acids it is as refractory as antimony. Toward alkaline solutions it is strongly resistant, while in water or in moist air it does not rust or corrode appreciably. It is known that antimony can be electroplated and gives a durable plating. It would be interesting to study tellurium in this direction. A systematic study of the available electrolytes that can hold tellurium in solution could be carried out advantageously. Antimony has been successfully used for many years in antifriction alloys and is an essential constituent of stereotype metal. No recorded study is known of an attempt to utilize tellurium in these alloys, but the whole field of the metallic alloys of tellurium needs to be studied carefully, and unquestionably an element whose general characteristics are so close to antimony will be found a useful metal instead of having no practical applications.

IRON AND STEEL—Another metallurgical line which has not been studied in any detail is the action of these two elements in the iron and steel industry. The effects of sulfur and phosphorus on iron and steel have been very carefully studied. The objectionable phosphorus has been most scrupulously removed by the basic open hearth process as a result of years of study and observations, yet to-day we are actually using iron phosphide to bring up the phosphorus content of open hearth steel which is to be used for certain purposes. It is interesting to contemplate what careful experimentation might develop on the influence of selenium and tellurium on the various grades of steel.

SELENIUM CELL—Selenium in the so-called metallic form has long been characterized by its unique action toward light. Its conductivity of the current varies so greatly when brought from the dark into the light that this peculiar property has caused the development of the selenium cell. This cell or resistance apparatus has found numerous uses at various times, such as automatically turning off city gas lights at daylight. It has been used in lighting and extinguishing the lights in light buoys, in army signaling of various kinds based on the heliographic principle, as a control in chemical processes such as the contact sulfuric acid manufacture, and in wireless telephones.

GLASS—It has been known for a long time that selenium gives a red color to glass. During the war this principle was made use of in decolorizing glass on account of the shortage of manganese. Selenium is introduced into the glass either in the elementary form or as a salt. As the rose color which it imparts is not exactly the complement of the green of ferrous iron, it is common practice to add a small amount of cobalt oxide along with the selenium. Since both selenium and its compounds are very readily volatile at such temperatures as are used in glass making, a large amount of the selenium decolorizer is volatilized. The loss of selenium is therefore high, and selenium can be used to decolorize glass only when the glass manufacturers are willing to pay the higher cost price. As soon as shipping was resumed after the war and manganese again became available the use of selenium in the glass business fell to almost nothing.

LITHOPONE—A number of possible uses for these elements suggest themselves, none of which have received the attention that they deserve. Lithopone, the intimate mixture of barium sulfate and zinc sulfide made by bringing together barium sulfide and zinc sulfate, is full of suggestions. Various colored lithopones can be produced by using an antimony sulfate liquor with barium sulfide, when the white barium sulfate is colored by the orange sulfide of antimony. Similarly, cadmium or arsenic liquors give a corresponding yellow lithopone. The substitution of selenium and tellurium is very suggestive, inasmuch as it should be possible to replace the sulfur of either the sulfate or the sulfide by either of these elements. The selenate and tellurate of barium are white and insoluble like the sulfate, while the selenides and tellurides like many of the metallic sulfides are variously colored.

MEDICINES—The use of the various compounds of selenium in medicine has received some attention, but the derivatives have had almost no systematic study. In a very careful study Prof. W. J. Gies, of Columbia University, has shown that tellurium compounds have a physiological action quite similar to that of arsenic but that their toxicity is much less. The selenides and tellurides as well as the oxidized salts have been experimented with in cancer, tumors, and syphilis, but their efficacy is more or less questionable. These few compounds which are of the simplest chemical character are almost the only ones of which any experimental results are recorded. When one considers the vast field of important and valuable sulfur-containing medicinals ranging from saccharin to sulfur itself and in the arsenicals from Fowler's solution to salvarsan, it would seem that there exists an almost virgin field for research by the physiological chemist. The offensive garlic odor of the "tellurium breath" will unquestionably act as a deterrent in the minds of some but should certain physiological actions be found, they might be so valuable as to overcome the objections due to the characteristic methyl telluride odor.

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[1] Report of a Committee of the National Research Council, presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

RUBBER—In the vulcanization of rubber a few experiments are recorded which seem to indicate the similarity of the action of selenium to that of sulfur. Much remains to be done, especially along the lines of the use of the chlorides or bromides of these elements as accelerators. Tellurium and its derivatives have received practically no attention in the rubber industry. Possibly from the nature of the organic materials present, the objectionable methyl telluride would again militate against its use.

DYES—A relatively small amount of research has been conducted with selenium in the dye industry while nothing has been done along these lines with tellurium. One of the first applications which would naturally occur would be the substitution of selenium for sulfur in the so-called sulfur colors, which are among our cheapest colors. There are at present two serious obstacles in the replacement of sulfur by selenium. The first is the relative cost of the selenium. The second is the nature of the bath which, in the present development of the sulfur color process, would make the cost prohibitive. There is, however, the possibility that there might be found a brilliant and fast color of considerable intensity which could be manufactured profitably. The field of synthetic dyestuffs possesses great opportunities for experiment and is almost undeveloped.

UTILIZATION OF RARE ELEMENTS

The utilization of the less common elements has always been a problem which has interested chemists. Not many years ago elementary silicon was sold at a high price per gram and even then it was almost a curiosity to be found wholly in museums, yet in combined form it comprises one-fourth of the crust of the earth. To-day silicon in elementary form is produced in large quantities at a few dollars per ton and is used on a large scale in deoxidizing non-ferrous alloys. Similarly a few years ago, tungsten was known only as a gray metallic powder with no other uses than that of the formation of the self-hardening steels. To-day the use of malleable tungsten wire in the lamp bulb and of the sheet metal in the spark coil to replace the more expensive platinum makes metallic tungsten a very important commercial product. Along the same line molybdenum, tantalum, and the oxide of zirconium are substances which until recently were only museum specimens but to-day are very useful products.

Only a few years before the war, large money prizes were offered in Europe for methods of utilization of bromine and of boron. We well know how valuable an element bromine was during the war and of the large consumption since the war, particularly in organic synthesis.

All of the elements which nature has furnished to us must find their place as a useful necessity to man. It is indeed incomprehensible that nowhere in the entire chemistry or physics of one or more elements is a single compound or property that cannot be utilized by mankind.

Except for the wartime use of selenium in the glass industry, the uses for selenium and tellurium are very limited. A few hundred pounds of each would supply all demands. The large amounts of these elements which are available to-day and for which there is no practical use have caused the National Research Council to create a committee on the Uses of Selenium and Tellurium. This committee, consisting of A. E. Hall, *Chairman*, with H. G. Greenwood, Victor Lenher, O. C. Ralston, E. W. Rouse, S. Skowronski, and A. W. Smith, has been working in close contact with the producers of selenium and tellurium in the United States, and it has been possible to make arrangements whereby large quantities of these elements can be secured at a very low figure for experimental purposes. The Raritan Copper Works, Perth Amboy, N. J., the U. S. Metals Refining Company, of Chrome, N. J., the American Smelting and Refining Company, Omaha, Nebr., and the Baltimore Copper Smelting and Rolling Company, Baltimore, Md., which include all of the producers of these elements in this country, will furnish workable quantities of these elements for research purposes at cost price.

Mr. E. W. Rouse, of the Baltimore Copper Smelting and Rolling Company, will ship at any time reasonable quantities of selenium to investigators, gratis, upon the recommendation of the committee of the National Research Council on Uses of Selenium and Tellurium, and Mr. Arthur E. Hall, of the Omaha Plant of the American Smelting and Refining Company, will forward reasonable quantities of tellurium, gratis, under the same circumstances.

CHEMICAL LABORATORY AND LECTURE ROOM AT THE WASHINGTON Y. M. C. A.

The rapid growth of the Science Department of the Washington Preparatory School, an integral part of the Association Institute, Y. M. C. A., made necessary larger and better quarters. A chemical laboratory and lecture room have accordingly been installed in the main building. These two large rooms are connected by a double door, and can be thrown together whenever desired.

Up-to-date equipment is provided to carry out work in elementary, analytical, and organic chemistry, and in photography. Recently the science apparatus of the Bristol School has been added to the equipment.

The lecture room is provided with a standard demonstration table and university chairs for forty students. A 40-inch blackboard extends along two sides of the room, the remaining space, exclusive of windows, being filled with wall cases, charts, and bulletin boards. Light and ventilation are afforded by large windows, but as the rooms are used more by the night school, special attention was given to artificial lighting. The Duplexalite system has been found very satisfactory.

The laboratory, designed for doing the work as expeditiously as possible, contains two tables for class work—a double center table and a single wall table. In addition, there are three marble-topped tables and a balance stand. The work desks were planned to accommodate twenty students, but it has proved necessary to assign two pupils to each desk.

The tables are fitted with 2-in. birchwood tops, finished by ironing in a mixture of paraffin and beeswax, thus retaining the beautiful grain of the birch and adding to the lighting effect. An uninterrupted view of the laboratory is obtained by omitting the usual reagent rack. Electric plugs for electrolytic work and for small motors are placed at intervals in the tables. Direct electric current is provided. Gas is piped to each desk by three-quarter-inch pipes tapped from a main 1.25-in. pipe.

The sinks are of soapstone fastened to three-quarter-inch galvanized pipe frames so placed that the tops of the sinks are 3 ft. from the floor.

Built-in wall cases for apparatus and chemical supplies, fitted with glass doors, add to the general appearance of the laboratory. All doors have friction catches and locks.

The frame of the 24-in. by 30-in. hood is of wood and the sliding sash is counterpoised by lead weights attached by means of hemp rope. Foul air is conducted through a flue to the top of the building.

A No. 35 Troemner balance rests upon a solidly constructed and securely fastened oak bench so that there is only a negligible amount of vibration from passing street cars. It is protected from dust and fumes by a glass case which fits over the balance and is secured by locks.

Opening from the main laboratory is a special dark room provided with benches, sink, cases, and lockers. This room is used in conjunction with the course in photography and for photochemical work.

In addition to the school library, a branch of the Public Library of the District of Columbia is housed in the school, making available a large number of books relating to chemistry and allied sciences.

A museum has recently been started by the presentation of a collection of minerals and several collections of specimens representing processes of certain manufactured articles. To these will be added other minerals and certain chemicals prepared by the students.

Instruction in chemistry is under the supervision of the Director of the Educational Department and the instructors are chemists well trained in their profession.

THE CHANDLER LECTURE

INTRODUCTORY REMARKS

By Ralph H. McKee
Columbia University, New York, N. Y.

In 1910 friends of Professor Chandler, mostly former students, presented to the trustees of Columbia University a sum of money which constitutes the Charles Frederick Chandler Foundation. The income from this fund is used to provide a lecture by an eminent chemist and to provide a medal to be presented to the lecturer in recognition of his achievements in science. We are gathered this evening to listen to the Chandler Lecture and it is my privilege to introduce the lecturer, Dr. Willis Rodney Whitney.

MEDAL ADDRESS

THE LITTLEST THINGS IN CHEMISTRY[1]

By W. R. Whitney
General Electric Company, Schenectady, N. Y.

To receive the Chandler Medal is to me doubly agreeable. My earliest interests in chemistry were largely influenced by what I heard as a boy about Professor Chandler and the Columbia School of Mines. At that time he was to me all there was of our science anywhere outside of Steel's "Fourteen Weeks in Chemistry." Through all of my lifetime he has been the American dean of chemistry. You may imagine my pride, then, in having my name thus connected with his.

But a second reason for my pride and pleasure is the fact that I live in the city which first recognized the qualities of Professor Chandler, and am a member of the board of trustees which paid him his first professor's salary. Therefore I shall show this medal at Union with elation. That he left our college to come to the Columbia School of Mines, where they paid no salaries, speaks well of Union, of New York, and of Professor Chandler.

In preparing an address which, while intimately connected with chemical affairs, might still be of interest to those who do not closely follow all its modern developments, it has been my aim to select a field in which great activity has recently been taking place. I have made no attempt to distinguish between chemistry, physics, and electricity in this connection, because the littlest things of the universe clearly belong equally to all three. Chemistry, physics, and electricity are coöperating in a thorough manner in their study of nature and it is evident that, from the viewpoint of this triple alliance, a wonderful new territory of interest has been opened. Possibly, also, by showing to the general public the exceedingly intimate relationships between the most theoretical and speculative parts of science and the highly prized technical applications, I may do something to encourage the younger men to appreciate the fact that the theoretical and speculative may be also truthful, spectacular, and valuable. I have made no effort to appeal to the expert research physicist, nor to write for those who are actually doing advanced research work in the line of the littlest things in chemistry, but rather to the much larger and, I hope, less critical group who are interested in seeing how much ado can be made about next to nothing. One may also quite properly maintain that there is no such word as "littlest." I may reply that there may also be no such *thing* as I talk about, but we get a great deal of satisfaction from thinking there is.

My object is to treat in a simple way some of the facts which we have learned more or less recently which have to do with our chemically fundamental materials. Different chemists occupying various fields of activity would handle the subject differently according as they are impressed with different applications. Physicists would treat the whole subject from quite another standpoint. The mathematician would introduce a third, the metaphysicist another, and so on. In the past, all have greatly advanced our knowledge. To most of us, these changing points of view are interesting largely in their application to some form of welfare work. I have had in mind the thought that I might talk about atoms, molecules, ions, and electrons, and still keep so well within the bounds of simple experimental demonstrations as to assist some of you in appreciating the applications. To those for whom such effort is unnecessary I would excuse myself by claiming a desire to help prepare the way for future students of the still more remote entity, the quantum, which it seems chemists must soon adopt.

It has always been natural to want to extend our vision. We have tried in vain to look through infinite space and to think through infinite time, though we know that we have no apparatus for such work. But, just as with telescope and microscope we have increased our knowledge within that portion which we may call our real horizon, without diminishing the incomprehensible total, so we have also advanced the frontiers of chemical or physical subdivisions (our metaphorical horizon), also without diminishing there the incomprehensible total.

Everywhere we look there still extends that distant arrangement of something we vainly call matter and energy which, because of our limited measuring apparatus, we still know only as infinite complexity. But what we can put behind us with weights and measures attached, we say we have added to science, and whatever has not been successfully weighed or measured we justly consider unknown. Thus chemistry first started to grow as a true and useful science when the balance came into use. So also psychology began as a science when it could be built even ever so little on experimental and measured facts. But when one of the world's greatest physicists tells us about things for which there are no generally useful measurements, or gives us data from untested balances, we seem justified in

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taking but passing interest. This will always be true in spite of the everlasting and infinite possibilities of future development. The more we realize the complexity and the detailed perfection of nature, which forces reverence and devotion from every true observer, the clearer we are that any specific knowledge which lies beyond the reach of our apparatus is available only through simple faith and therefore, fortunately, equally to all, regardless of apparatus.

Not long ago, we thought of the atom of matter as a hard, round, indivisible something beyond which we would probably never need to look. The molecules were made up of such atoms more or less bonded together and still with more or less freedom of motion. This limited freedom accounted, for example, for the greater amount of heat required by complex molecules to raise their temperature than required by simpler molecules. But nowadays the atom has become a regular solar system. Nothing is capable of explaining its properties, discovered in recent years, short of removing from it all the simplicity it was supposed to have, and adding to it such new complexities as only incomprehensible celestial systems possess. This additive appreciation of matter apparently without reduction of the still unknown remainder will always proceed, but there are reasons for each step, when taken, because there is developed the new apparatus for measuring the added appreciation.

It may seem strange that many of the facts which led investigators to discard the former ideas of hard atoms have come from studies in a vacuum. There, where we might expect the least, we have found the most, and there, where now we ought to be able to say we have a clear understanding of all possibilities, we must admit a still infinite field of unknowns.

Willis Rodney Whitney, Chandler Lecturer

As so many things have happened *in vacuo*, I will approach the general subject of the little things along this path, which ought to offer fewer obstructions. The kinetic theory of gases came to be something better than a theory and was a useful collection of coördinated facts with known laws, before we knew that at least a part of our indestructible atoms were going to pieces. Thus while our theories have some of them become more nearly laws, some of our laws have been repealed. In these affairs, however, facts have not suffered and the facts about the properties of atoms, for example, are the same old facts, only they are augmented by new increments. In other words, what we gain by our measurements usually remains, while what we think with preconceiving thought may disappear.

Without blushing, we nowadays refer to the number of molecules of gas per unit volume and know that whatever complications they may individually involve, they are separate and discrete and numbered accurately. When they change their number by the effect of temperature or because of chemical activity, when some break down and others combine—we also know and count the effects. Never before was the belief in little particles called molecules so firm. The theoretical conceptions of atoms seem to have become the clearest of facts. The early ideas were not bold enough, though they were rightly aimed. The subdivisions of matter below the atom and down to the ion and electron are as certain as anything we know, and now energy itself in the quantum hypothesis is being given a minimum dimension. These results have come, not by mathematical or theoretical speculation alone, but through simple direct experiments.

SUSPENSIONS IN LIQUIDS

In approaching the littlest things we may well start with suspensions in liquids. For example, sand in water seems simple and yet much of the most complex phenomena of solutions can be found in this analogy. When the sand is fine enough, yet visible under the microscope, its suspended particles are always in a dancing sort of motion. We say this is due to the impacts of the invisible molecules and that the whole combination is in thermal equilibrium; also that the average kinetic energy of all the particles is the same. What we say of the sand is true of all sorts of finely divided material, solid or liquid, and the finer the visible particle the greater its amplitude of motion. Ultramicroscopes, while still incapable of disclosing molecules, disclose an ever-greater activity of all suspended matter the finer the state of its subdivision. The tendency of the sand to settle completely is so counteracted by this individual motion of the particles that the final state of balance is one in which the concentration of the suspension varies with the height in the liquid. At this point any further settling is opposed by what we call the increased osmotic pressure of the suspension. This enabled Perrin to calculate from visible suspensions the cocnentration of molecules or the number in any volume. His result agrees with that obtained from other methods, but this method interests us most as seeming most simple and direct. The suspended sand is also found to be electrically charged and so resembles the ions of an electrolyte. Under the influence of an electromotive force the particles migrate in one or the other direction. Evidently the amount of charge per particle need not be a single unit and its sign may vary with the nature of the solution.

COLLOIDS

As the particles get smaller and approach atomic magnitudes the electrical quantities are more easily measured. The suspended particles act like dissolved salts. Positive colloids are precipitated by negative colloids just as the much smaller ions, silver and chlorine, precipitate each other. Albumen in an acid solution is positively charged and is negative in an alkaline solution, as though the charge was determined by absorbed H and OH ions. The tendency for aggregates to form by the union of dissolved or suspended matter and electric charges is a general phenomenon which is clearly shown when moisture is precipitated where air is ionized. In a soap solution McBain has shown that large suspended particles made up of aggregates of the hydrated fatty-acid radical exist as negative particles just like the sand particles, while the sodium or potassium exist as positively charged but single and separate atomic ions. Here we have in one solution a mixture of crystalloid and colloid electrochemical elements. This state, though last to be discovered, might have been predicted from the charged atoms of the ions of Faraday and the charged colloidal suspensions of Graham and Hardy. A refinement of simple microscopic methods has carried our power of distinguishing particles of suspended matter down so close to the accepted dimensions of molecules that we must claim to have optical evidence of colloidal particles of *some* elements like gold and silver, which are actually smaller than the molecules of some other substances. This refinement is merely an extension of the method we employ in observing the dust in air traversed by a beam of light. Using concentrated light and ultramicroscopes, molecular dimensions and visible subdivisions of matter have been brought closely together.

DIMENSIONS OF MOLECULES

Chemists who have absorbed from their first lessons the idea of molecule and atom have felt the necessity of seeing in equal volumes of different gases just the same number of molecules, because of the volume relations in gaseous reactions. They have also sensed the van der Waals equation, which mathematically expresses the fact that if we compress a gas made up of discrete particles, however small, we finally reach a point where they individually object to being further crowded. When pressed too closely they go out of the gas state and into the liquid or solid, and there it is measurably much harder to compress them any closer together. These facts, through their mathematical expressions, long ago led to fairly definite conclusions as to number, size, and motions of the molecules of a gas.

Everyone probably accepts the relative rates of diffusion of different gases through porous walls as a sign of differences in molecular sizes, and we would look for the relatively high diffusion rate of hydrogen as compatible with its small molecular dimensions. This diffusion process is apparently yielding wonderful fruit at present, in showing that our particularly anomalous element, chlorine, with its unsympathetic atomic weight, is probably a mixture of two or more elements (isotopes) which have never before been separated. It has been through the studies connected with the smallest particles of matter that we have been led to try to separate such permanent old elements as chlorine into components.

Without attempting to give exact numbers I may say that there are nearly 30 billion-billion molecules per cubic centimeter of air under ordinary conditions, and that when the first practical incandescent lamps were evacuated, they still contained over a million-million molecules of air. Before we proceed to smaller dimensions I want you to get a closer view of the common molecules and some conception of their size. We are familiar with the sand on the seashore and it has long served as a measure of number. Assume that the grains average one-one-hundredth inch in diameter, a million could then fill one cubic inch. Let them represent our molecules. On this basis the molecules in a glass of water would suffice to cover the United States with such sand grains one hundred feet deep. We are forced by our measurements to accept such results before we can go further along this line.

STUDIES IN VACUO

For forty years we have been continually devising new means of producing high vacua, not because the very highest is needed in a good incandescent lamp, although it is, but because the further we went the more interesting became the results. With each new type of vacuum pump a few million more molecules were removed from the bulbs. This in turn usually called for a new apparatus to measure the new vacuum and so the frontier over against nothingness was extended. It seems strange at this late day to say that probably the best vacuum we can permanently maintain and accurately measure still contains over two billion molecules per cubic centimeter: that is, there are still one hundred times as many molecules in a well-evacuated lamp as there are people in the world.

DISTILLATION IN VACUO—With the candid acceptance of the gas molecules as real things, whether hard or soft, it was surprising how many physical facts became obvious. Such a simple observation as distillation of metal *in vacuo* is a case at point. If a metal such as copper is distilled in a glass bulb, as by boiling it from a relatively infusible electrode or vaporizing it by an arc, it will be seen condensed on all parts of the walls, but, if this takes place in a fairly high vacuum there will be clean shadows formed on all shaded surfaces of the glass. In other words, the copper distils in straight lines, and even a fine screen remote from the glass will produce a sharp shadow. This is all in accord with the fact that at ordinary pressures the path of such vapor-molecules is very short and there is so much mechanical interference that no shadows can form, but with the air molecules out of the way, the mean free path of the copper molecules, at its low pressure, exceeds the dimensions of the bulb itself and practically all the copper distils in straight lines.

GAS FLOW—Another interesting case is that of the rate of flow of a gas from a bulb into and through a capillary. When the vacuum is fairly high, so that the molecules of gas have a long average path free of interference with one another, the rate at which they will pass out of the bulb and into the capillary is determined by the number which can strike on a surface of the bulb corresponding to the area of the capillary, and this is small. This means that at low pressure the rate of removal of a gas is very slow. For example, for a liter of gas at a millionth atmosphere pressure to pass out through a tube 1 mm. in diameter and 10 cm. long would require over 15 min. if it were going into a perfect vacuum. A molecule can enter the capillary only when it is aimed just right. If the area of its bulb is a million times that of the capillary there is only one chance in a million that it will leave the bulb on any round trip across it.

EVACUATION—It is worth while in this connection just to mention the changes which have taken place in apparatus for producing high vacua, because without such improvements it would be impracticable to produce even those we now commercially require. Moreover, the new pumps, because of their method of operation, all conform to the requirements of the kinetic theory of gases. For high vacua the old reciprocating pump and the rotating oil pump are not enough. The so-called molecular pump of Gaede was an improvement. This is essentially a high speed revolving disc of metal, fitting so closely into a case or covering that the molecules of gas may be said to be bumped along in the direction of rotation. It marked a great advance. In the later diffusion pumps the gas to be removed is carried away by mercury vapor, into a stream of which vapor it is diffusing. In neither of these pumps are there any of the plungers and valves which are common to older pumps and which seriously limit the velocity and quality of the evacuation.

ELECTRONS

We will now see how the studies in vacua led to submolecular magnitudes. In the early days of vacuum lamps Mr. Edison noticed the peculiar fact that from a hot filament a low current would always flow to a metal plate located within the lamp. This soon became known as the Edison effect. It was peculiar and not clearly understood, but he showed that this current flowed only one way; that is, the plate always became charged negatively, just as though negative electricity flowed from the hot filament to the cold plate. This was before the day of known electrons and there was no thought of using the phenomenon in the still undiscovered wireless and X-ray work as we do to-day, but the observations were published.

It was not until we had become hardened to the conception of small mobile charges of electricity that the chemical significance of such phenomena began to appear.

Now we look at everything as made up of two kinds of electricity and we find this added peculiarity: the negative kind is everywhere a collection of one little unit with the same characteristics, from whatever source it is drawn. On account of its existence as the essential part of all matter, we are greatly interested in its properties. By its study, great progress is being made and the promise for future help is unlimited, though the work is scarcely begun.

With the demonstration of the theory that gases are actually made up of molecules, the objection to considering other discrete particles, such as electrons, was reduced, and there is now a definite tendency to apply all the gas laws to the electrons. We think of a metal as containing many electrons per atom, and we consider the electrical conductivity as due to the motion of these electrons. We look upon a hot metal as surrounded by a layer of negative electrons and when we apply a high negative voltage to the metal they shoot away from it. This is the source of the Edison effect.

Sir William Crookes was the first to realize this as a state of matter, which we now call a stream of electrons. He observed in his vacuum tubes the negative or cathode ray which, first thought of as residual gas molecules electrically charged (and called by him a fourth state of matter), was finally conceived as made up of negative electric charges smaller than atoms. These electrons have a mass corresponding to about one-eighteen-hundredth of the hydrogen atom, which mass is due to and varies with the velocity.

ELECTRON MASS—J. J. Thomson's name is inseparably connected with the determination of the mass of the electron, the charge which it carries and the velocity of its motion. Produced in different ways in different gases or from metals *in vacuo*, by heat or by photoelectric effect, the properties of the electrons were found the same. They were counted by counting the particles of fog they could produce. Their charge was measured by the electric current which they could carry, and they were weighed and their velocity determined by their deflection in magnetic and electrostatic fields.

CHARGE—It had long been believed that atmospheric air contained a few carriers of electricity, just as the purest distilled water does, because neither one is a perfect electrical insulator. In Dr. Millikan's wonderful experiments on the rate of fall of small oil drops between electrically charged plates, he showed not only that the air contained some of these ions and that from time to time one was taken up by his oil drop, thus altering its rate of fall, but he also showed that the number of these charged ions in a given volume was reduced by partially evacuating the space and also that many more were produced in the air by the action of X-rays or radium rays. Moreover, as his oil drops were originally charged with a number of these units of electricity, it was probable that the friction produced in atomizing the oil had called forth on the oil drops some of these ions. This connects for us in an interesting manner the oldest electrical phenomenon of frictional electricity and the newest phenomenon of ionization of air by radium or X-rays. It also makes a new road for experiment because it indicates that there are several simple ways of separating the same electrons from all kinds of matter and studying them and what they leave behind. This work has apparently proved that when the ancient amber is rubbed a few more negative electrons are rubbed from the cat's skin than from the amber and thereafter they merely perform the antics of regular standardized electrons. They may be counted and branded without alteration and are always the single identical little negative units of electricity. By quantitative observation Dr. Millikan accurately determined the amount of negative electricity which we must ascribe to each of the electrons—47,740-millionths absolute electrostatic units.

ELECTROLYSIS—When the current passes between copper plates in copper sulfate solution, copper passes through the solution as positively charged atoms or ions, while the sulfate ions with negative charge carry current in the opposite direction. This is easily measured, and the work of Faraday gives us the quantitative relationships for such transport. While the charges per monovalent atom are the same as our electrons, these electrons do not occur separately from the atom in the solution and an electrolysis should, therefore, tell us the number of atoms in a volume of electrolytic gas. Perhaps the hydrogen electrolysis is the simplest illustration. Hydrogen forms with chlorine hydrochloric acid. It gives to the chlorine its negative electron and is thereby left positively charged; the chlorine becomes therefore negative. In the aqueous dissolved state the ions of hydrogen and chlorine are acting independently as influenced by the electric potential. As electrolysis takes place the hydrogen positively charged atom recovers at the electrode a new negative electron and becomes ordinary atomic hydrogen. If now we compare the quantity of hydrogen gas obtained by our electrolysis with the quantity of electricity put into the process, assuming that each hydrogen atom takes one electron, we find that per gram of hydrogen gas produced there are required about 60,000 billion-billion electrons and that therefore there are this number of atoms of hydrogen in one gram or about 30×10^{22} molecules. Since the gram corresponds to about ten liters of hydrogen, we may say that the cubic centimeter contains about one ten-thousandth of this or thirty billion-billion molecules. This value, measured by electrochemical means, agrees with that obtained by entirely different methods and fixes the electrochemical electron as the electron of our vacuum tubes and decomposing elements.

LUMINESCENCE—The fourth state of matter in the Crookes tubes is now the cathode ray composed of these ever-present negative electrons. When a beam of these electrons is directed at low velocity against various chemical compounds, characteristic luminosity is produced which we know as fluorescence and phosphorescence, but when the impelling voltage is high enough, the velocity of the motion o' these electrons is so great that their sudden stoppage by impact within the atoms of matter produces the short waves which we call X-rays. These are characteristic of the internal structure of the material of the target of the X-ray tube. Thus, as will be seen later, we have gained much new information about the inside of atoms from X-ray studies. To repeat: A highly heated metal *in vacuo* emits negative electrons. These constitute a current which will flow in one direction only (negative from the hot surface to a cold one). This fact has become very important in a number of fields. It constitutes, for example, the simplest way to procure very high voltage direct current, as the production of high alternating voltages is simple and of this energy the thermionic vacuum tube will permit current to flow only in the one direction.

WIRELESS—In its simple form of one hot filament and a cold electrode *in vacuo* this arrangement is called a valve tube. The valve tube is one of the most important pieces of apparatus connected with wireless communication. In one form, at the receiving station, it serves to let the high frequency oscillating current from the antennae pass in a single direction only so that the telephone may be usefully affected. In another case it is used at the receiving station as magnifier or amplifier for the feeble current available. This case involves the direct control of a stream of electrons (a sort of cathode ray) by the interposition across the path of the rays of the delicate varying voltage received from the antennae. This effectively controls, triggers, or dams back a much greater current of electrons which are supplied by a local source of power. In this way the slight variations of a feeble circuit control a much more powerful local circuit and thus act as multipliers of the wireless energy. This is using the electrons in accord with their known laws and, in fact, by the same static principle by which the mass and velocity of such electrons were determined by J. J. Thomson. This free handling of the electrons has led also to their use in the same form of vacuum apparatus, as generator of a current of high frequency from any source of alternating electrical energy. This oscillator, which still uses only the moving electrons *in vacuo*, is connected to an electrical capacity and inductance so that the potential of the energy rises and falls at a rate depending on the impedance to its flow and the capacity of its temporary containers, much as water in a U-tube may be made to oscillate in height when the rates of flow are properly controlled. Thus there are already a great number of technical applications of the properties of the free atomic fraction we call the electron. Although we know it in our arcs, our rectifiers, our X-ray tubes, our audions and pliotrons, the field has apparently only been scratched. With increased knowledge of electronic peculiarities we may expect greater advances in more complex environment than in our simple vacuum tubes or in the gaseous state. Naturally the phenomena of chemical action and the solid and liquid state must offer a great field for new study in this direction.

GAS IONIZATION

When gas is present in the bulb with the hot electron-emitting cathode, the impact of these negative electrons on the gas molecules in some way breaks these latter down into other new negative electrons and positively charged remainders. It is now known that each atom of an element contains a definite number of these negative electrons. The number varies in regular order throughout the periodic table of elements. This process of ionizing is the separation of one of these electrons from the atom, the remainder of the atom being left with a positive charge including most of its original mass. This ionization produces an increase in conductivity of the path and serves as an explanation, which we had long needed, of the fact that the electrical resistance of air quickly diminishes automatically on starting an arc, and an air-gap at once becomes a short circuit, unless outside resistance is used to place an upper limit to the current to be permitted.

Owing to the special properties of argon at pressures of a few centimeters of mercury, the current-carrying power of the hot-filament rectifier is enormously increased through the presence and ionization of this gas; so that, instead of only a few milliamperes at a very high voltage, it becomes possible to obtain several amperes at a few volts rectified current. That is, the peculiar chemical nature of argon, owing possibly to the structure or arrangement of the electrons composing it, makes it fit well where no other gas will do as well. Thousands of rectifiers with this combination of thermionic emission and argon ionization are now being used commercially to charge storage batteries from alternating circuits. The older mercury rectifier is also a case of this kind.

ELECTRIC ARCS

In connection with arc-lamp studies, I have lived through all apparently possible changes in the views on the phenomena of electric arcs. In the early days there were men who thought that the electric current flowed in conductors in the positive direction, that is, as though it were made up of positive charges. Thus the early investigators looked for a passage of positively charged material of the electrode across the arc, and thought they found it. This seemed to represent the action of the carbon arc because the carbon anode wasted away much more rapidly than the cathode. Both were burning up in the air, however, and the anode being hotter, burned more rapidly. *In vacuo*, on the other hand, it became evident that the phenomenon was quite complicated because simple distillation masked any regular electrical transport of matter. This was also finally found to be the case with metals used as electrodes. For years there seemed to be no rhyme or reason in the material losses of arcing electrodes of any kind, whether these be burned in air, *in vacuo*, or under water. Much research work was devoted to this subject. It was of the greatest technical importance. Our views are now simpler, if not really simple. We know that arcs in chemically inert gases may be burned indefinitely without loss of either electrode. Weight losses occur only through direct evaporation (when the heat is not carried away fast enough by conduction) or through the combustion of the electrode.

All these facts are illustrated by the commercial arc lamps of to-day. In the carbon arc both electrodes waste away. In the magnetite arc only one wastes away and that very slowly. In the mercury arc, where the mercury is really a non-consuming but necessary cathode, and in such arc lamps as tungsten in argon or mercury vapor, no change of either electrode occurs. We believe that even in this case negative electrons cross the gap and their impact on the anode heats it, while the cathode has to be heated externally to produce the starting electrons.

ATOM CONTENT

We have been forced, then, to recognize the electrons as part of all atoms. They are negative charges of exceedingly small mass but all alike. When one of these leaves an atom there remains a positively charged mass differing from the original neutral atom in this charge and in a very slight mass reduction. Thus we picture something much more complicated than hard, round atoms. In the first place most of the volume of the atoms has all the properties of empty space. A very small part apparently carries all the useful attributes. This view was forced upon us when it was shown that positively charged helium atoms may be fired through other atoms without apparently coming into contact either with electrons or the residual nucleus, except exceedingly rarely. It is this penetrability with its infrequent collisions which leads to the following enlarged picture of relative dimensions in atomic structures. We must apply the microscope to our grains of sand. A fair way is to start with the simple hydrogen molecule, which is the smallest, and examine one of its atoms. Other atoms will be similar but not simpler. The hydrogen atom may be looked at as consisting of one standard negative charge or electron balanced by a positive charge or nucleus. As we need some mechanism to keep these two charges from merging entirely, it seems necessary to adopt the celestial orbit with motion about the center of gravity. The atom, if spherical, has a diameter of about one one-hundred-millionth centimeter and the single electron a diameter four one-hundred-thousandths as great. The nucleus, which is thought of as near or at the center of the orbit of the electron, is very much smaller than the electron itself. We may say that, using the atom diameter as one mile, the electron would look like a baseball at the end of the half-mile radius and the nucleus would be a positively charged pinhead at the center of the circle. Moreover, this pinhead represents about 99.5 per cent of the total weight.

There is much experimental evidence that the hydrogen atom can thus be best conceived of as a little solar system with the electron rotating about the nucleus. For example, there is a series of many lines in the hydrogen spectrum which have very striking mutual numerical relationships. These are such that they could all be produced by the shifting of electrons from orbits greater than the least by simple successive multiples. That is, electrons which are driven out of their orbits by the electrical disturbance which produces a spectrum are thought of as giving the spectral lines by their orderly return to their natural orbit about the nucleus. The different lines correspond to the motion of the electrons in passing from exterior orbits back to the unit orbit. The lines show by their wave-lengths that these orbits bear the relation to the unit orbit of the squares of the simple whole numbers 1, 2, 3, 4, etc.

The above Balmer spectral series of hydrogen would then be produced by the return of the baseball from different orbits after having been displaced to double, triple, etc., its normal distance from the atom center. The innermost orbit, as disclosed by the spectral lines, agrees in dimension with the over-all dimensions of the hydrogen atoms, otherwise determined. Some such thing seems probable when we accept the fact that the gas has to be electrified, *i. e.*, the atoms ionized or the electrons split off, before it can become luminous or produce any spectrum.

This again is a picture which conveys the thought that hydrogen at least is mostly space, and that therefore this is probably true of everything. This in turn contradicts no known facts, as the properties for which we have a sense of appreciation like hardness may be given us by the stability of these little solar systems.

No excuses are offered for the mechanical pictures we draw. They have always been drawn in chemistry and experience has shown that, whether true or false, progress is made through them. When X-rays and radium were discovered it seemed that the bottom had dropped out of our elementary conceptions. Additional quantitative experiments have shown, however, that we always possess at any time only an incomplete picture. Chemists always hoped to see some form of Prout's hypothesis proven, although they have thought for a century that no justifiable data were available. They tried to build all matter from one protyle stock, but failed. Yet nowadays the thing seems almost demonstrated. Everyone who had studied thermochemistry knew that the elements in any recognizable state whatever, even at the absolute zero of temperature, contained energy, and that what we measured in thermochemical processes were only differences. But even with this view we were surprised when an element was found which gave off heat and decomposed continually, thus making us wonder about the others. We are now going to be forced to learn the energy content of each atom.

X-RAY SPECTRA

If the present condition teaches anything, it is that we are in the midst of a most interesting period of chemical development. That different elements must possess complicated internal mechanisms in order to render any understanding of ordinary spectra possible has been recognized since Bunsen's day. Modern X-ray studies promise to make this problem clearer.

Each element, when its atoms are struck by electrons (cathode rays) at high enough velocity, emits a characteristic line spectrum, the wave-lengths of which vary progressively and by regular intervals from element to element throughout the entire series.

No artificial story of any plot yet untested by literature could be more striking in human interest than this discovery by young Moseley, the Englishman who was unfortunately killed at Gallipoli in 1915. He did more to simplify all our elements than anyone else has ever done. For a century or more we had known ordinary spectral lines without being able to understand them. They differed enormously from element to element and good men spent their lives studying them. Then the X-ray was shown to consist of light waves 10,000 times shorter than ordinary light, but there was still no apparent way of producing interference, diffraction, or spectra. The wave-lengths were so short that no grating could be ruled for them. Yet it was natural to try to produce an X-light spectrum. This was accomplished through a wonderful conception of Laue in 1912, that the almost infinitely small atoms which are spaced regularly in all crystals might be there arranged in such fine structure that they would do for X-light what the finest possible rulings of Rowland or the thin film of an iridescent soap bubble had done for ordinary light, *i. e.*, produce a spectrum. A great hope was thus realized. The distribution of the energy of the total radiation of X-light could be disclosed by spreading out the different wave-lengths just as they are spread in an ordinary spectrum. Moseley, in studying these spectra, which contain characteristic lines of relatively great brilliancy, discovered almost the first relationship of importance which we have obtained of any kind of spectrum. What Moseley showed, put into simple form, was that the spectra of our chemical elements, produced by using them as sources of X-rays, differed one from another in a very simple, progressive, numerical manner. The spectral lines of one chemical element were found shifted a definite amount into shorter wave-lengths for the spectrum of the element of next higher atomic weight throughout all the elements tested. This, in its regularity, was even more striking than our periodic table, because it was not periodic but progressive and suggested simple synthesis of elements. It gave us every reason to believe that our lightest known elementary atom contained one electron and that all other elements were derived one after another by the addition of one of these identical units of electricity. Naturally, since the atoms are electrically neutral, this means that the positive charge on the nucleus also increases by one unit for every additional electron. Thus the highest element of the series (uranium) contains 92 electrons and all elements fall in order between 1 and 92.

This is like saying that everything in the universe (because we know that all celestial and terrestrial elements lie within the same range) is made up of different collections of the same little electrical bricks, that all numbers up to 92 are in use, but that none are more complex than number 92. Moreover, all except five of the possible atoms with electron numbers between 1 and 92 correspond to well-known elements. Five unknowns may yet be discovered.

The analogy with ordinary light is quite perfect in the case of X-rays. Because of their exceeding smallness, electrons fired at high velocity into a surface set into motion corresponding components of the atoms. These small electric charges thus vibrating and recovering their proper places cause the characteristic short wave of X-light. This corresponds to the ordinary light of longer wave-length which a mass of matter gives off when bombarded mechanically (as by friction) until red-hot. It is not surprising therefore that the internal mechanism of the atom can to a certain extent be disclosed by the X-ray spectrum.

Without going too far into X-ray spectra, I want to refer briefly to the subject of crystal analysis, because that again is of the greatest chemical interest. We have always known of the crystallizing tendencies of many substances, without knowing whether everything crystallized or not. We have often wondered what determined the regular forms which most elementary and compound substances persist in assuming, how some substances possess more than one crystal form and so few possess identical forms. It also seems as though matter showed among its various crystalline forms about all the regular shapes geometrically obtainable. It is now becoming evident that our crystals are structures in which the atoms determine the form and unit dimensions by the natural distribution of their electrons, and it is entirely unfair to talk of a molecule of a crystalline substance at all, because any one atom is equally related to more than the molecule conception permits. The atoms are arranged in brick-like regularity with distances between atom-centers of the dimension of the previously demonstrated atom-size. This the X-ray has shown.

It has been shown experimentally that a selected beam of X-rays, on passing through the powder of a crystal, will produce on a photographic plate a group of lines or pattern corresponding to the form of the crystal and to the elements of which it is composed. In other words, it looks as though every crystalline substance was distinguishable from every other, even when in powder form, and that mixtures could be analyzed by the lines of these X-ray patterns.

DECOMPOSITION OF ATOMS

In considering the atom I chose hydrogen, the smallest, and said it was mostly empty space, except for one negative electron and a still smaller nucleus. This little negative unit seems to meet us everywhere, whether in the electric current of a wire, the thermionic emission of a hot body, the ionization of a gas or the conduction of a current through aqueous solutions. Probably one of its most striking appearances is as a free electron shot spontaneously from certain atoms, which thus indicate that they are too complex to exist indefinitely. With negative and positive charges as building stones the elements may be built up or torn down. For from Moseley's work it became evident that the atoms of the elements differed progressively one from another by the presence of added pairs made up of electron and positive charge. The chemist's periodic table taught him that the characteristic properties of the elements, such as valency, resided in the electrons of the outer portions or shell of the atom which probably rise in number successively from zero to eight, as indicated by the groups of eight in the periodic table. This leaves the rest of the electrons in each case as a part of an inner core or nucleus. While there may well be some errors in the literature concerning the spontaneous decomposition of the heavier elements, it now seems very sure and quite acceptable that uranium, thorium, radium, and actinium are shooting out negative electrons and positively charged ions and changing accordingly into elements of lower complexity. Thus the heaviest elements of the chemist's category gradually fall back into more stable forms, but disclose in doing so only negative electrons and positively charged helium atoms. These are the β- and α-rays of the radioactive elements. In this process it need not surprise us therefore to find an X-light (the γ-ray) produced during this electronic discharge. The effect of electrons upon the material of targets in the ordinary X-ray tube indicates that X-rays identical with the radium γ-rays might be expected when the impinging electrons have a speed corresponding to several hundred thousand volts. X-ray tubes are usually operated below 100,000 volts, but the decomposing radium corresponds to higher voltage and so its electrons produce shorter wave-lengths.

QUANTA

With electronic conceptions we also begin to see some relation between such phenomena as the photoelectric effects, the decaying elements and thermionic emission. What radium, uranium, etc., do at any temperature equally well, potassium does when illuminated and all materials when sufficiently heated; that is, they all emit the same negative charges, the electrons. Thus the photoelectric cell is another one of those relatively insignificant things, which, like the decomposing element and the electron whose mass varies with its velocity, seem about to force us to important changes in our views as to the little things.

We have long known that when light falls on certain metals, particularly sodium, potassium, and lithium *in vacuo*, a current of small magnitude flows negative from the metal; that is, the metal gives off negative electrons. This resembles the Edison effect referred to, but it takes place from a cold metal and is independent of the temperature. The energy displayed by these fired electrons is apparently not obtained from the incident light, though this would be the logical conclusion. This seems unsatisfactory because the velocity of the escaping electrons, the force with which they are fired, is determined by the frequency or wave-length of the impinging light and not by its energy. A feeble energy seems to serve to shoot an electron with a force entirely out of proportion to any actual energy which could have been collected by the electron from the light. Even when we pass from ordinary light through ultraviolet to X-rays the same thing seems true. A beam of X-rays striking metals or even gas molecules causes them to send out negative electrons with very high velocities corresponding to the very short wave-length of the X-rays. Moreover, the electrons shoot at once apparently without waiting for light energy to accumulate locally sufficiently to account for this energy of motion. The thing happens just as though the metal already contained a lot of electrons loaded for firing, the energy being stored except for the triggering effect of a little energy of corresponding frequency. There seems perfect analogy in this case between ordinary light on metals causing electron emission at certain velocities and X-light causing similar electron emission of much higher velocities.

This may not be so bad if it is true that the elements have in them billions of times more energy than we have formerly considered. This energy is disclosed by the radioactive elements in their decomposition. It becomes a question of the mechanism of the discharge of the electron with this stored energy, and how it happens that the discharged electron assumes a velocity corresponding to the frequency of the incident light waves. This calls for the emission of energy in units or quanta instead of continuously. It makes us look for some mechanism like resonators differing in different elements, but something which can account for a discontinuous system of emission and absorption of radiant energy.

Again, one of our greatest interests lies in chemical reactions. How do they proceed? We know from experiment how the temperature affects their velocity and are therefore not mentally disconcerted by explosions, nor surprised that Dr. Loeb finds the velocity of life in fruit-flies 300 per cent greater at 30° C. than at 20° C.; but we are bothered to explain the fact that we have various but fixed rates of first-order reactions instead of instantaneous processes.

Why should some of the molecules of a given gas react when others do not? Something must give some of them what Marcelin calls the "critical increment" necessary for their activation.

W. C. McC. Lewis has suggested that this energy is taken from space by some mechanism which responds only to definite oscillation frequencies, which are determined by the molecular structure. He believes that the reception of radiant energy as shown by absorption spectra of the reacting substance is the criterion, and that the individual molecule reacts when it receives a single quantum of energy of the particular frequency. This is the energy unit $h\nu$ now generally accepted in radiation, where ν is a frequency and h a universal electronic constant.

In the case of the quantum relationship we also find support in the present view of the production of light in the line spectra of hydrogen. The lines are due not to the regular orbital motion of electrons, but to the definite finite steps taken by the electrons in passing from outer to inner orbits. This makes it a little easier to get the conception of radiation units as required by the quantum relationship. The light is not continuous but is emitted in units $h\nu$, where ν is the frequency and h a constant. In general, an electromagnetic disturbance, a moving energy wave in space, has been imagined as produced by speed changes (not by regular motions) of electrons. If these are finite and their speed change finite, the resulting energy emission might be expected to be formed of finite energy units like the quanta.

It is not my intention to try to bring you to the very brink of the precipice of the entirely unknown. Some chemists and physicists must, with clear vision and unnatural perspicacity, work there, and continue to peer beyond the really visible. They must form new theories to coördinate the recently discovered facts which will then direct the search for still better understanding and further knowledge.

To the chemist, however, there is soon bound to come a great deal of new help from the studies of the structure of the atoms.

As indicated above, this work might be thought of as started by Mendelejeff's periodic system. There the electropositive and electronegative natures of the elements were arranged in order as functions of mass and the chemist hoped to find all elements made up of protyle units. But Sir William Crookes gave atomic composition its real pathway when he showed that substances *in vacuo* at high voltages all shoot out the identical kind of negative electric particle. The electrical relationships were then made still more evident by the discovery that the positively charged gas particles carry practically all the atomic weight. Thus in low vacuum apparatus these two kinds of matter or electric charges could be studied. Through the analyses of rays of moving negative electrons and the corresponding positive ions now easily obtainable we are thus led to see more clearly a lot of little things which were heretofore indistinct.

STRUCTURE OF ATOMS

The special activities of electrons in atoms is naturally a matter of great interest. There is so much accumulated information on the properties of elements, chemical and physical, that, having a conception of the number and identical character of the electrons, some useful picture of their arrangement in space seems possible. The first successful picture in this attempt was that of Bohr, which I have touched upon. Roughly stated, he pictured the electrons in their stable state as rotating in concentric circular orbits about a positive nucleus. Certain applications of external energy, like electrical bombardment, may disturb this state, but the tendency is then for the electrons to return to their proper orbits. In this act of returning from a remote but simply related orbit luminous radiations are produced. Thus the lines of the element's spectrum are conceived to be produced by the orbit-to-orbit motions of electrons, and this is in accord with the ideas we have of characteristic light-wave production.

In the case of hydrogen, as given above, there was a remarkable confirmation of the Bohr conception because, after his original publication, a new series of hydrogen spectral lines was discovered, and these, in conformity with the theory, are produced by the electron in returning to the innermost possible orbit for the hydrogen atom. The two other series, Balmer and Paschen (infra red), correspond quantitatively to the return of electrons from outer orbits to the second and third natural concentric orbits, respectively. Thus the positions of a large number of lines constituting at least one element's spectra are calculable on the assumption of regular concentric ring orbits having simple diameter relations of the squares of ascending numbers beginning with unity.

It need not surprise us to find the complications much greater when we come to more complex atoms and we are evidently not very near a good method for calculation of the spectra in general.

For the chemist it has seemed more satisfactory to try to place the electrons in stationary and geometrically regular positions in the atom, and at present this need not necessarily interfere with the conception of motion of the electrons in hydrogen and helium, for example. It seems also quite possible that a perpetual orbital motion of all electrons in atoms may be made compatible with the fixity which the bonds of organic chemistry demand, by considering as the fixed points of attraction the centers or foci of circular or elliptical electronic orbits.

By confining the electrons to simple, regular, geometric positions in spherical shells, many of the chemical and physical regularities are coördinated. G. N. Lewis and Langmuir have studied this subject with valuable results. In this way the limited but varying valency of elements is made clearer and what we like to call reasons for the chemical activity of elements, their positive and negative natures and the inactivity or neutrality of such others as the argon group, are coördinated. For example, the inert gases are conceived as having in their outer shell a maximum or equilibrium-number of electrons which accounts for their inactivity. A natural tendency towards this type of structure for maximum stability is also looked upon as the reason for the chemical properties of the other elements.

VALENCY

All the elements differ one from another in the number and arrangement of their electrons. This difference is expressed in the Mendelejeff table, for we have long recognized countless properties occurring with periodic regularity. It is no strain to our imagination, therefore, to picture the relative stabilities of aggregates of electrons as periodic functions of their number and even to find that eight is a peculiar key-number. If shells of eight are most stable, then both higher and lower numbered shells will be less stable and there will be a tendency for a group of nine to give up an electron and of seven to take on a new one. This conforms to the highly negative nature of fluorine, the well-known stability of neon, and the positive nature of sodium, which in accord with Moseley's work have 7, 8, and 9 electrons, respectively. If this is a true picture, then we may as well attribute affinity to these electron differences and see in the dissociated form of sodium fluoride, for example, the liberality of the sodium with its one extra electron in accommodating the special avidity of fluorine for just that one electron. This leaves the sodium as a positive ion and the fluorine as a negative one. Two fluorine atoms may be looked upon as bound together by the tendency of each to complete an octet, which they do by sharing a pair between them. In this way chemical reactions and electrolytic dissociations are brought about through the tendencies of the electrons concerned to rearrange themselves in the most stable possible relationship with one another. This particular subject evidently merits much better attention than I can give it and I shall be satisfied if I have given you even a slight desire to follow it further.

ISOTOPES

Some of our well-known elements are automatically going to pieces and others are having decomposition thrust upon them. Was there ever a more important period in the history of chemistry? The first proof of this atomic disintegration was the radical discovery that radium was a new, uncontrollable, and dangerous element which was shooting itself to pieces. This story of radium is another of those countless truths obtained through novel and distinctly quantitative measurements and orderly research, by which our powers of appreciation seem overtaxed. To many such things we seem at first to turn a dulled edge of appreciation in order not to get big nicks in the sharper side of our senses. How could it happen that, with our countless tons of old, reliable, available elements, we should have to get our greatest lesson from an element of which the whole world contained hardly enough for a necessary atomic weight determination? The answer as usual is found in quantitative measurements. The idea that the atom of one element became the atom of another, by losing helium and negative electrons, had to be accepted, because there was no other acceptable interpretation of measured facts. Thus radium was shown to be decomposing by the discharge of relatively large, positively charged particles now known as helium nuclei of atomic weight four, and by the discharge of negative electrons of relatively negligible mass. These were the original α- and β-rays of the literature, the γ-rays are the X-rays due to the subsequent actions of the β-particles. As the loss of the positively charged helium atom from any element meant a reduction of four in its atomic weight the question at once arose as to what is wrong when, in the orderly decomposition of uranium through radium and polonium, we reach a point where the residual atom must have an atomic weight of exactly 206. Lead appears at this point in our old table with a weight of 207. It must have taken great faith to suggest that ordinary lead was a mixture. It called for further accurate work on atomic weights. Fajans and Soddy could predict this element with an atomic weight of 206, and it had to be found in ordinary lead. No one was so well fitted for critical atomic weight work as Richards, therefore those most interested turned to him. In 1914, he, together with Lembert, showed that lead from different sources certainly varied in atomic weight far beyond any possible error in manipulation and that ordinary lead is a mixture, one of whose components has a weight of 206. Elements composing such mixtures, previously considered single elements, are now called isotopes. This was another big little thing in chemistry which has done more for knowledge of atomic structure than anything within a century. It has opened the mind of the physicist and chemist to expect the unexpected and to take up again the apparently eternal search for the ultimate possibilities of nature.

CANAL RAYS

Just as the negative electron had its mass determined through its deflection by a magnetic field, so the masses of the various positive ions have also been measured. The positive ions so far studied are the residues of gaseous molecules from which one or more negative electrons have been detached by electrical means. They were studied by Thomson, Wien, and others in the space behind the cathode of a conducting Geissler tube. To handle them by themselves they are allowed to pass through a hole in the cathode towards which they are directed by the electromotive force. This beam, quite analogous to the cathode beam of negative electrons, is called the canal ray or positive ray. Under the simultaneous influence of static and magnetic fields placed at right angles to each other, these ions describe parabolic curves which are recorded photographically, and thus the positive ions of which the positive ray is composed were found to correspond in mass to the respective atomic and molecular weights of the gases in the space.

This is another of those wonderful developments which was started by a single almost insignificant and remote study of an atomic fraction. It is to-day leading us chemists to revise entirely our most elementary conceptions. It is another big littlest thing. From the self-recorded curves of the positively charged ions of many of our presumably simple gases we are obtaining, through Thomson's work, entirely new light on their composition. In ionized nitrogen, for example, there are found single atoms of nitrogen with one and two positive charges and some nitrogen molecules with two and even three atoms sharing a single positive charge, but there is nothing but nitrogen present. Aston, continuing this work, is finding that some of the supposedly elementary gases are mixtures of isotopes. Argon, for example, may become a mixture of an element of exactly 40 atomic weight with a few per cent of another element of 36 atomic weight. Neon, whose atomic weight was supposed to be 20.2, has been definitely proved to consist of two closely allied elements of exactly 20 and 22. Aston has thus determined over forty atomic and molecular weights by his refinement of the positive ray method, and has found that without exception every one is a whole number.

Thus the study of positive ions has led to the discovery of an entirely new field of phenomena in atoms, where the most refined measurements by physical and chemical means will be necessary. The indications are that even our old intractable chlorine is to be split up into a mixture of isotopes of 35 and 37 atomic weight. Evidence is therefore accumulating that all the real atomic weights are practically whole numbers and that the apparent fractional weights are due to various mixtures of elements which in turn have whole-number atomic weights.

Among the foremost in these opinions are Rutherford and Harkins who would build all the elements, even helium itself, out of the stuff in hydrogen; or, since this in turn is a positive nucleus and a negative ion, out of hydrogen nuclei and electrons.

Rutherford believes he has actually produced the hydrogen nucleus from nitrogen by bombardment of nitrogen with helium nuclei, for, in this way, he obtained charged particles whose path-length was four times that of the helium nucleus and corresponded with that obtained by similarly decomposing hydrogen gas. No other explanation fits the facts.

Harkins has discovered that the elements of greatest abundance are of even atomic weights and are practically exact multiples of that of helium. As this stability might be expected, compared to atoms with odd atomic weights, from stability data of radioactive decomposition, he likes to consider the helium nucleus as the weight basis of all the simpler elements of even atomic weight below nickel, and to see in the odd number atoms the additional mass of three hydrogen nuclei.

Such elements as do not seem to correspond to this point of view will at least have to undergo a critical investigation as to their right to exist.

The positive nucleus is apparently the seat of what we call the atomic weight because the mass of the electron is insignificant compared to it. If these nuclei are built up of hydrogen nuclei, all atomic weights will be its simpler multiples. Even with due consideration of probable isotopes, this does not exactly satisfy all the atomic weight data. The step now being taken is to look for the necessary weight corrections in the principle of relativity. This expresses mass as equal to the energy divided by the square of the velocity of light. The internal energy is evidently there in the atoms; and its quantity, if due to or housed in the electrical charges, might be slightly different, in the case of an atom containing positive charges closely arranged, from that of the energy of the same charges separated.

The magnitude of such corrections, due to the relativity principle, seems to be of the proper dimension, and this will force the chemist to study relativity.

Whether we like it or not we are proceeding along the path of new theory. We are producing new mechanical conceptions patterned after old ones, but pushed farther. One cannot see the end. There will be none. Starting with what we feel we know, if we are wise, we will always try to extend it. What we knew of molecules could for a while be measured by what we would expect from very small solid balls, but that period did not endure. Now, by reducing the size of the components and by making them electrical, we have driven the centers of all properties into smaller common corners without making the final understanding any more simple, though it is more orderly. The electron now has to do, in less space, much more than the atom formerly did, because we have found new regularities of nature, such as cathode rays, decomposing elements, etc. All the properties of matter are accredited to the smallest conceivable spots where the slightly understood negative electricity, in formerly unsuspected indivisible units, holds itself at a definite and respectable distance from positive electricity with which it has always previously been considered as annihilating itself. Its motions must produce light and carry heat. Its immobility must account for cohesion and strength of materials and its collected and arranged groupings must determine all the differences of material with which we are familiar. And yet we do well thus to force the issues. This may be proved by the fact that our chemistry has been built up in this way and without it no orderly, forward-looking chemistry seems possible.

PRESENTATION OF THE MEDAL

By Charles F. Chandler

New York, N. Y.

It is my privilege to present to Dr. Willis Rodney Whitney the Chandler Medal. I appear as the representative of the more than 500 of my old pupils and other friends who in 1910 established this Foundation in honor of their old professor. One of these founders graduated as early as 1847, and several others during the succeeding years prior to 1864 when I began with Professors Egleston and Vinton to teach in the newly founded School of Mines.

I was deeply gratified when I learned from Professor McKee that the distinguished Dr. Whitney had consented to deliver the annual lecture. The name is dear to me, and suggests a possible blood relationship between us. My mother was a Miss Whitney of Boston.

Dr. Whitney was born at Jamestown, N. Y., on August 22, 1868. He graduated at the Massachusetts Institute of Technology in 1890, receiving the degree of S.B. In 1896 he received the degree of Ph.D. at Leipzig. He has been most successful as a teacher of chemistry, having filled the following positions at the Institute of Technology:

1890–1892: Assistant Instructor in Sanitary Chemistry
1892–1894: Instructor in Sanitary Chemistry
1898–1901: Instructor in Theoretical Chemistry and Proximate Analysis
1901–1904: Assistant Professor in Theoretical Chemistry
1904–1908: Non-resident Associate Professor of Theoretical Chemistry
1908– : Non-resident Professor of Chemical Research

Since 1900 Dr. Whitney has been the Director of the Research Laboratory of the General Electric Company at Schenectady, and during the war was a member of the Naval Consulting Board and director of research work at Washington. Words and time fail me to give you any adequate idea of the number, variety, and importance of the researches which have been successfully conducted by him and his willing assistants and associates during the past twenty years. Some idea of the magnitude of his activities can be realized from the fact that he has developed the research laboratory at Schenectady from its inception till now he has more than 150 persons working with him.

It would require a series of lectures to lay before you an adequate account of the various important results which have been developed under Dr. Whitney's direction. The first radical improvement in the carbon incandescent filament since Edison first produced it was due to Dr. Whitney's personal work. The "Gem" lamp which he developed with its "metallized" filament, embodying a new form of carbon, gave 25 per cent more light with the same wattage than the standard carbon filament lamp. Still greater improvements resulted in his laboratory when the drawn wire of tungsten gave us the "tungsten lamp," then the gas-filled half watt lamp. Then in arc lighting the laboratory developed the magnetic electrodes, and produced the most successful arc lamp of to-day.

Did time warrant, I would gladly tell you about numerous other wonderful discoveries and inventions in the practice of the industrial arts which Dr. Whitney has suggested and inspired in his twenty years of research work, and also remind you of the numerous scientific papers he has published in the journals.

Dr. Whitney's successful labors have been recognized by his fellow scientists. He is a member of the following societies:

The American Chemical Society (President in 1909)
American Electrochemical Society (President in 1912)
Society of Testing Materials
American Institute of Mining Engineers
American Institute of Electrical Engineers
Société Chimique de Paris
American Academy of Arts and Sciences
American Physical Society
British Institute of Metals
American Association for the Advancement of Science

Now, Dr. Whitney, permit me to present to you, as representative of the president and trustees of Columbia University and the more than 500 alumni and friends who established this Foundation in 1910, "The Chandler Medal," in recognition of your wonderful and successful labors in the application of physics and chemistry to the industries of this country.

SCIENTIFIC SOCIETIES

NEW YORK SECTION, SOCIÉTÉ DE CHIMIE INDUSTRIELLE

The meeting of the New York Section of the Société de Chimie Industrielle was held in the auditorium of the Chemists' Club on Friday evening, May 14, 1920. Prof. M. T. Bogert, of Columbia University, presided in the absence of the chairman, Dr. L. H. Baekeland.

The opening address of the meeting was delivered by Hon. Maurice Casenave, chairman of the French High Commission to the United States. After hearty words of congratulation to chemists for the splendid part they had played during the war and with expression of the hope that the same talents and energy would be devoted to the solution of the problems of peace, M. Casenave paid a glowing tribute to the prompt work of reconstruction and rehabilitation now in progress in France. He emphasized the necessity of France producing more and importing less in order to stabilize its exchange. He gave an interesting account of the development of water power now in progress in France and expressed the hope and belief that within five years the hydroelectric developments in France would reach a total of five million horse power which would make France no longer dependent upon outside countries for its coal supply. A vivid picture was painted of the difficulties of transportation which had handicapped the shipment of potash from Alsace.

In introducing the second speaker, Mr. Joseph H. Choate, Jr., the presiding officer emphasized the important bearing of the coal-tar chemical industry upon our potentialities in chemical warfare. Mr. Choate held the close attention of his audience by his effective presentation of the commercial methods used by the Germans against the chemical industries of this country before the war. He gave in detail the activities of the Germans in seeking to prevent in this country the manufacture of salicylic acid, oxalic acid, potassium bicarbonate, aniline oil, and bromine. From the Hearings before the Senate Committee, he read an extract from an article by Mr. C. H. Burr in the July 1919 number of the *Quarterly Review*, in which Mr. Burr, after describing in general the pre-war status of German business in the United States and describing in outline the system of graft commonly in practice, gave an account of a "convention called under the cartel" at which the convention entered on its minutes the following resolution:

> *Resolved*, That henceforth bribery shall be abolished, except in the United States and in Russia.

Mr. Choate also called attention to an article from the October 1919 issue of the German journal *Chemie* in which it was stated (*translated*):

> So far as the chemical industry is concerned, let me say, in the first place, that the aniline dye industry and the pharmaceutical industry have now so thoroughly recovered that there can be no thought whatever of outside financial assistance. Even to-day the German chemical industry is again in a position to take up at once the leading role in the world's markets.

He also read from a prospectus put out by the Badische Anilin & Soda Fabrik Co. in which were given the details of the large increase in workmen employed by this company as compared with the number employed during the war or prior to the war.

In conclusion Mr. Choate said that all chemists should urge their senators to vote for the legislation now before the Senate providing adequate protection for the coal-tar chemical industry.

The following officers were elected for the ensuing year:

President: Marston T. Bogert
Vice President: J. Enrique Zanetti
Treasurer: J. V. N. Dorr
Secretary: Charles A. Doremus

The members of the Council consist of the following:

Jerome Alexander
L. H. Baekeland
Charles Baskerville
Henri Blum
Charles F. Chandler
René Engel
Georges de Geofroy
Ellwood Hendrick
Charles H. Herty
George F. Kunz
W. H. Nichols
G. E. Valabrègue

SIXTH NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES

The National Exposition of Chemical Industries returns to the Grand Central Palace in New York, where it will be given during the week of September 20 to 25, 1920, inclusive.

This year's Exposition will be more pretentious than ever; in fact, it will be the largest distinctly industrial Exposition ever held. There are now engaged for the coming Exposition 358 exhibitors. The growth of this Exposition has been remarkable, and in a way indicates the growth and development of the chemical industries in America. In 1915 the first Exposition was composed of 83 exhibitors, the second increased to 188, the third to 288, the fourth to 334, and the fifth, in which the available space was much restricted and exhibitors were held to a minimum, admitted 351 exhibitors. The present number of 358 the managers tell us cannot be much increased because of the limited amount of space remaining. Another floor has been added, giving four floors of the Grand Central Palace, each of which covers a whole city block.

Quite as remarkable as the growth of the Exposition itself is the increased attendance and interest that is shown in the exhibits. To the first Exposition there came 63,000 visitors, to the second 80,000, and this has steadily increased till at the last the attendance exceeded 111,000. One who has watched the development of the Exposition and the interest of the visitors can testify to the great improvement in character of representatives the manufacturers have in attendance with their exhibits and the whole-souled way in which they give valuable information and discuss the details of the nature of the many materials on exhibit. On the other hand, the exhibitor profits doubly from this open contact with the men from the field, for often the suggestions they make are immeasurably valuable and the orders they place equally as welcome. The visitors, too, have undergone a change—one of education. The first Exposition brought forth a small following of the idly curious, but in subsequent Expositions a study of those attending has developed the fact that the interest of even the general public is more vital. These are the people whose minds and confidence are being trained now for the future development of the chemical industries. Those in whom the exhibitor is primarily interested for the business he must do, come in large numbers. An unusually large attendance from all over the world is expected at the Sixth Exposition.

This year there will be three special sections: the Electric Furnace, the Fuel Economy, and the Materials Handling Section. The two latter are new sections. The first will, as its name implies, be one of electric furnace exhibits; the Fuel Economy Section will consist of exhibits of machinery and apparatus, furnaces, producers, stokers and all devices for the economic utilization or more efficient combustion of fuel. The possible exhaustion of our fuel reserves in the not far distant future and the present high cost of fuel make this section one of much interest to all industrial plants. The Materials Handling Section will be a series of exhibits of machinery and equipment for the handling of material, such as conveying, transporting, elevating, and included in this will be weighing, measuring and power transmission equipment. So important have these mechanical features become for all industrial plants due to the shortage and high wage for man-power that an unusual interest is expected in this new section.

The program for the Exposition will have sessions on subjects the phases of which will be developed in the exhibits of these latter two sections. There will be sessions on chemical engineering for which an elaborate program is planned. Motion pictures which will have a keen interest for technical men will form part of the program, and there will be popular public addresses as well.

REPORT OF THE DYE DIVISION OF THE AMERICAN CHEMICAL SOCIETY

At the St. Louis meeting twenty-one papers were presented to the chemists present, of which three were read by title.

The attendance reached a maximum of sixty, but it is estimated that a total of one hundred attended the meetings at one time or another. The by-laws for the Dye Division were read and unanimously approved. As the council of the AMERICAN CHEMICAL SOCIETY also approved these, they became the official by-laws of the Dye Division.

The chairman, Dr. C. L. Reese, appointed a nominating committee, which reported the following gentlemen as nominees for next year's officers: Mr. A. B. Davis, *Chairman;* Mr. W. J. Hale, *Vice Chairman;* and Mr. R. Norris Shreve, *Secretary.*

No other nominations were made, and, on motion duly made and seconded and unanimously passed, the secretary was instructed to cast a ballot for the above-mentioned gentlemen. The chairman then declared these men duly elected to take office at the close of the present meeting.

The chairman appointed to the executive committee of the division Dr. C. G. Derick and F. B. Holmes. These with the members *ex officio* make the personnel of the executive committee as follows: A. B. Davis, W. J. Hale, R. Norris Shreve, C. G. Derick, F. B. Holmes.

NEW YORK, N. Y.
April 29, 1920

R. NORRIS SHREVE, *Secretary*

ASSOCIATION OF SCIENTIFIC APPARATUS MAKERS OF THE UNITED STATES OF AMERICA

The Second Annual Meeting of the Association of Scientific Apparatus Makers of the United States was held at Washington, D. C., Thursday and Friday, April 22 and 23, 1920, and was attended by thirty of the leading manufacturers of scientific instruments, analytical balances, chemical glassware, optical instruments, and pyrometers.

The purpose of this Association is to improve the construction and design of the scientific apparatus of this country and to standardize the same so as to get uniform quality and sizes; also, the most important object is to build up in the United States a precision instrument industry that will be of aid to the National Government in time of emergency. Prior to 1914, practically all instruments of precision were imported and when our Government declared war in 1917, it was found that there were not enough instrument makers and manufacturers to provide adequate supplies of precision instruments for the laboratory control of essential factories and to build fire control instruments for the Army and Navy. The Association is now working to perpetuate this industry and to make the nation independent of any foreign country. In carrying out their program they are working in conjunction with the National Research Council, AMERICAN CHEMICAL SOCIETY, Bureau of Standards, and the various scientific bureaus of the National Government.

One of the most important addresses of the occasion was given by Dr. S. W. Stratton, director of the Bureau of Standards, in which he set forth the various activities of the Bureau and stated how it would be possible to coöperate with this Association. On Friday afternoon, at the invitation of Dr. Stratton, the Association was shown through the various departments of the Bureau of Standards.

Committees were appointed on standardization in the various departments to work in conjunction with the above-mentioned agencies and also, if possible, to correlate their work with the committee of the Society of Chemical Industry of Great Britain, which is working along similar lines. There was also a committee appointed on publication which will report later.

The officers for the coming year are as follows:

President: M. E. Leeds, of Leeds & Northrup
Vice President: H. N. Ott, of Spencer Lens Company
Secretary-Treasurer: J. M. Roberts, of Central Scientific Company

SOCIETY OF COTTON PRODUCTS ANALYSTS

The Eleventh Annual Convention of the Society of Cotton Products Analysts was held at the Grunewald Hotel, New Orleans, La., May 10 and 11, 1920. There were over seventy-five members present, and many interesting and valuable reports and papers were presented.

The membership committee reported a total membership of 202, an increase of forty-nine during the past year.

In the report of F. N. Smalley, chairman of Coöperative Work, the check meal work of the past season was discussed and the conditions under which it should be continued were decided.

It was brought out that this work was conducted at a cost of over one thousand dollars, and that there were eighty who received and analyzed the series of forty samples. General improvement was shown and remarkable uniformity of results on several of the meals mentioned.

The prizes offered for the past year were won as follows: *Moisture Cup*, L. G. Forbes, Little Rock Laboratories, with an average of 97.17; *Oil Cup*, G. C. Hulbert, Southern Cotton Oil Company, Augusta, average 99.28; *Ammonia Cup*, G. C. Hulbert, average 99.58. The second leg of the Grand Prize Cup was also won by Mr. Hulbert with average of 99.43. This is the second year it has been won by Mr. Hulbert.

The report of W. D. Richardson, chairman of the Moisture Committee, brought out the opinion that any loss by heat method was not accurate and that the efforts to secure an accurate method should be made in another direction than by drying in any type oven.

A description of the Eastman colorimeter was presented by Dr. Wesson, and the Bureau of Standards new instrument was shown by Dr. I. G. Priest, associate physicist. Both are to be investigated thoroughly by the Color Committee and it is hoped that between the two instruments one can be selected to replace the Lovibond tintometer.

The Society made several important changes in its constitution, which include a change of name to the American Oil Chemists Association. It is the endeavor to insure the accuracy of all analyses of cottonseed products which become part of contracts or arbitration by the formation of an examining board, who will examine all commercial chemists and issue certificates to those who pass the examination. The provisions to carry this out were added to the constitution and a committee of five to be elected by the governing board will shortly start on the work of preparing the conditions of examination. It is believed that this is the most important work that the Society has ever attempted and that its successful completion will mean the decided improvement in the already high-class work that is done by the commercial chemists of the trade.

The meeting closed with a banquet at Hotel Grunewald, at which an address by H. E. Howe, National Research Council, on the relation of the National Research Council to our Society was decidedly the feature. Mr. G. Worthen Agee, retiring editor of the Chemist Section, Cotton Oil Press, Memphis, Tenn., was presented with a token of appreciation of the work he had done for the Society.

The following officers were elected for the ensuing year:

President: F. B. Porter, Fort Worth Laboratories, Fort Worth, Texas
Vice President: C. D. Cluff, American Cotton Oil Company, New York
Secretary-Treasurer: Thos. B. Caldwell, Law & Company, Atlanta, Ga.

ANNUAL MEETING OF THE CHEMISTS' CLUB

The Annual Meeting of the Chemists' Club was held in the rooms of the Club at 50 East 41st Street, New York City, Wednesday evening, May 5, 1920. The program of the evening was divided into three parts—a preliminary dinner, the business meeting, and a delightful entertainment.

President Ellwood Hendrick presided at the business meeting and at the outset gave a resumé of the accomplishments of the Club during the past year and the hope for the coming year. The address of the president was received with enthusiasm by the members of the Club.

Various officers read detailed reports of their activities, all of which showed that the Club was in an extremely sound condition. The treasurer reported a financial condition better than in any previous year. The secretary quoted an increase in membership and the acquirement of a considerable amount of Chemists' Building stock. The Club now owns more than 40 per cent of the outstanding stock of that company.

As a result of the ballots, the election of the following officers was announced:

President: Ellwood Hendrick
Vice President: Resident, William F. Hoffmann; Non-resident, Victor G. Bloede
Secretary: J. R. M. Klotz
Treasurer: H. M. Toch
Trustees: F. J. Metzger and T. R. Duggan

One of the important acts of the meeting was the passage of a resolution placing in the hands of a voting trust the Chemists' Club's stock of the Building Company. The resolution was as follows:

> *Resolved*, That the Trustees be instructed to establish a voting trust for the stock of the Chemists' Club Building Company, now held in the treasury of the Chemists' Club, or which may hereafter be acquired by gift or purchase; such a trust to consist of three members of the Chemists' Club who shall exercise on its behalf the voting power appertaining to said stock. They shall be appointed by the Trustees of the Club to serve for terms not exceeding five years each, but the service of a member as voting trustee shall not preclude him from succeeding himself if the Trustees of the Club reappoint him to the office.

The following distinguished chemists were unanimously elected honorary members of the Club: Giacimo Ciamician. H. LeChatelier, John U. Lloyd, William H. Nichols, Edgar F. Smith, Ernest Solvay, T. E. Thorpe, and Edward Weston.

Considerable discussion arose over the question of purchase of a four-story building adjacent to the Club and now under lease to the Club. No definite conclusion was reached.

For future elections it was determined to have a nominating committee to replace the present method of nominating by ballot. It is hoped that this change will result in a larger number of nominations of officers and trustees of the Club.

Congratulations are due to all of the officers of the Club for the successful conduct of its affairs during the past year. The Club is proving itself more and more of a necessity, not only for the chemists resident in New York City, but more especially for non-resident chemists who find in the Club so congenial an atmosphere for their place of residence during their visit to New York.

WILLARD GIBBS MEDAL AWARD

The tenth award of the Willard Gibbs Medal was made by the Chicago Section of the AMERICAN CHEMICAL SOCIETY on Friday evening, May 21, 1920, to Dr. Frederick G. Cottrell, assistant director of the United States Bureau of Mines. In connection with the presentation of the medal, a reception and dinner were held, following which Dr. Willis R. Whitney presented the medal. The subject of the address of the evening, by Dr. Cottrell, was "International Scientific Relations."

CALENDAR OF MEETINGS

International Conference of Pure and Applied Chemistry—Rome, Italy, June 15, 1920.

National Fertilizer Association—27th Annual Convention, White Sulphur Springs, W. Va., week of June 21, 1920.

American Society for Testing Materials—Annual Meeting, Asbury Park, N. J., June 22 to 25, 1920.

Forest Products Laboratory Decennial Celebration—Madison, Wis., July 22 and 23, 1920.

American Institute of Chemical Engineers—Semi-Annual Meeting, Montreal, June 28 and 29; Ottawa, June 30; Ontario, July 1; Shawinigan Falls, July 2; La Tuque, July 3; Chicoutimi, July 4; Quebec, July 5, 1920.

Society for the Promotion of Engineering Education—Annual Meeting, Ann Arbor, Mich., June 29 to July 3, 1920.

American Chemical Society—Sixtieth (Annual) Meeting, Chicago, Ill., September 7 to 10, 1920.

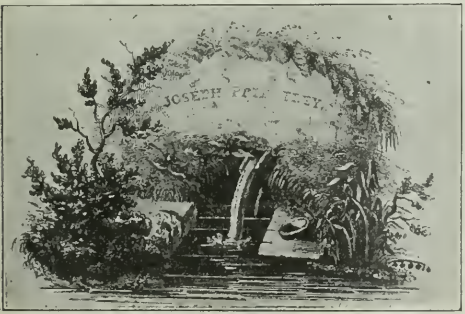
Sixth National Exposition of Chemical Industries—Grand Central Palace, New York, N. Y., September 20 to 25, 1920.

NOTES AND CORRESPONDENCE

THE BOOKPLATE OF DR. JOSEPH PRIESTLEY

Editor of the Journal of Industrial and Engineering Chemistry:

In connection with the revival of interest in Joseph Priestley among American chemists, as shown by the appointment of a Priestley Memorial Committee by the AMERICAN CHEMICAL SOCIETY and by the announcement of the removal of the Priestley House in Northumberland to the campus of the Penn State College, the following reference to the bookplate of the distinguished discoverer of oxygen may deserve a notice. I have seen no mention or reproduction of this plate in any of the biographies of Priestley.



The original plate from which the accompanying photograph was made is in one of the books that formed a part of Priestley's library which was pillaged during the Birmingham riots of July 1791. It will be remembered that Priestley, as a dissenting clergyman and sympathizer with the French revolution, had aroused the animosity of a fanatical mob which, over a thousand in number, burned Priestley's church, plundered his house, destroyed the apparatus of his laboratory and scattered his books and manuscripts to the winds. Priestley and his family barely escaped with their lives. Some of the books in Priestley's library were afterwards recovered, yet many valuable works were lost. Priestley in a letter[1] written over a year later states that one of the most disagreeable circumstances attending the riot with respect to his recovered books was that the sets were almost all broken.

The book which bears the plate has lately come into the writer's possession from England and is entitled "The Laboratory or School of Arts," a translation of a German collection of receipts for working gold, silver, etc., and published in London in 1738.

The plate was engraved by Allen of Birmingham and represents a stream of water gushing through a spout from under a massive rock into a smooth glassy pool. A stone curb, overgrown with grass and flowers, surrounds the spring, on one side of which lies a cup for the convenience of the thirsty wayfarer. The moss-covered rock above the pool has carved upon it the name JOSEPH PRIESTLEY.

For simplicity and charm the writer has seen no bookplate which surpasses this one. For a chemist who worked so much upon the composition of water, the theme of the engraving is most appropriate, while for those who have drawn inspiration from the life and works of Priestley, and who have watched the streams of progress which trace back to his early efforts, the symbolism of a fountainhead has an added significance.

> "At once the fountain, stream and sea;
> They were—they are—they yet shall be"

NEW YORK SUGAR TRADE LABORATORY, INC.
80 SOUTH STREET, New York City
May 10, 1920

C. A. BROWNE

TWO LETTERS ON A NEW TYPE OF CONDENSER FOR THE DETERMINATION OF CRUDE FIBER

Editor of the Journal of Industrial and Engineering Chemistry:

In the March number of THIS JOURNAL, 12 (1920), 288, Mr. C. A. Clemens describes what is doubtless an efficient reflux condenser for use in determination of crude fiber.

Referring to numerous previous condensers, he says, "The latest and best of these is the one designed by Howell D. Spears."[1] I can all the more heartily agree with that statement for the reason that the condenser which Mr. Spears designed and described in 1919, I described in 1910, and designed and used some years previously.[2] This is the language used in that description:

> Fig. 1 (accompanying illustration) shows the manner of digesting the fiber: A beaker 7 to 8 cm. in diameter, about 15 cm. deep, capacity 600 to 800 cc., covered by a round-bottom flask through which flows cold water. Any convenient number of such digesters may be connected in series by rubber tubes 25 to 30 cc. long, and the water run through the series from first flask to last. There is no loss of digesting liquid by evaporation; and if the boiling is started and conducted slowly, no great trouble from foaming, since each digester may, without disturbing its neighbor, be lifted and swirled.

There are, of course, minor differences between Spears' device and mine—the main one being that the cooling water passes into and out of my flasks through tubes in doubly perforated stoppers in the necks of the flasks; whereas his tubes are fused in.

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[1] Bolton's "Scientific Correspondence of Joseph Priestley," Letter No. 78, p. 130.

[1] THIS JOURNAL, 11 (1919), 140.

[2] *Ibid.*, 2 (1910), 280.

But I am bound to say—such is vanity—that if anyone will turn to THIS JOURNAL, 8 (1916), 366, he will find a description of a crude fiber digestion plant which, while as efficient as others in preventing evaporation and checking frothing, is incomparably superior in durability, compactness, ease of operation and economy (in the long run) of construction. Round-bottom metal condensers take the place of flasks, rubber connections are entirely dispensed with, the cooling water does not pass from one condenser into another and finally into the drain, but through each condenser separately direct into the drain. The bottoms of these condensers need not, of course, be round; they might be flat or slightly convex and each provided with a half dozen, more or less, drip points. But since they are already efficient, why this additional complexity? J. M. PICKEL

FEED LABORATORY
NORTH CAROLINA DEPARTMENT OF AGRICULTURE
RALEIGH, N. C.
March 17, 1920

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Editor of the Journal of Industrial and Engineering Chemistry:

The first part of the criticism offered by Mr. Pickel to the paper appearing in the March number of THIS JOURNAL, 12 (1920), 288, deals mainly with a question of priority between Howell D. Spears and himself. The points which seemed, at least to us, of advantage over the condenser described by Howell D. Spears,[1] and consequently over the condenser of Mr. Pickel, have already been pointed out.

Undoubtedly the metal condenser which Mr. Pickel describes is very excellent and efficient. There are, however, advantages for both types. The copper-zinc condenser requires special plumbing and resolves itself into a more or less permanent fixture in the laboratory, for which many laboratories cannot afford to devote space. The glass condenser can be quickly and easily set up and taken down. The fact that the copper-zinc condenser, as long as it does not come in contact with acid, is more durable than the glass apparatus is evident, but there is an opportunity for difference of opinion in regard to Mr. Pickel's statement that it is "incomparably superior" in compactness and ease of operation. Mr. Pickel speaks of "additional complexity," when his metal condenser is as complex as the glass condenser, and is also incomplete in itself while the glass condenser is complete.

FOOD AND DRUG LABORATORIES
STATE OF SOUTH DAKOTA
VERMILION, S. D.
March 30, 1920

C. A. CLEMENS

INDUSTRIAL CHEMISTRY AT COOPER UNION

The Cooper Union for the Advancement of Science and Art, New York City, has announced a new day course in Industrial Chemistry opening in October 1920. The course will cover a period of four years. During the college year 1920–21 only first-year courses in General Chemistry and Qualitative Analysis, Mathematics, Physics, and English will be given. It is intended that the instruction provided shall be eminently practical and thoroughly scientific and that it will furnish adequate equipment for young men and women who desire employment as analysts, production foremen, research chemists, engineers, factory superintendents, purchasing agents, and in other phases of industry which call for persons with chemical training. At the same time the course will provide a proper foundation for original research and productive scholarship in industrial lines.

The course in Industrial Chemistry as offered will include a fundamental training in general, analytical, organic and physical chemistry, as well as extensive acquaintance with technical industrial operations involving chemistry. It will also include supplemental equipment in mathematics, physics, mechanical engineering, electrical engineering, economics, and English needed to make its graduates fitted to hold positions of trust and responsibility.

Applicants who can furnish certificate of graduation from a four-year day course in an American high school will be admitted without examination. All others will be examined in algebra, geometry, English and history on September 15 and 16, 1920. Personal and physical examination, to be given September 23 and 24, will be required of all applicants. Preference will be given to those applicants having previous technical experience.

The course will be under the direct supervision of the head of the department of chemistry of Cooper Union, Horace G. Byers. He will be aided in its development not only by the staff of the department and such additional instructors and lecturers as may be necessary, but also by Dr. Maximilian Toch, recently appointed Adjunct Professor of Applied Chemistry in Cooper Union.

Applications for admission may be made in person at the office of the Cooper Union or by mail up to September 13, 1920. A circular giving the ground covered by the examinations may be had upon request. No tuition fees are charged by Cooper Union.

A NEW METHOD FOR THE DETERMINATION OF SULFUR IN OILS

Editor of the Journal of Industrial and Engineering Chemistry:

Two days before the receipt of the May number of THIS JOURNAL, in which a paper with the above title appeared (pages 482 to 485), the author came across the description of an essentially identical method.[1]

Goetzl treats the oil, in a platinum crucible, with fuming nitric acid, evaporates off the excess, mixes the oily residue with soda and saltpeter, covers with more of these salts, and fuses directly over a burner without stirring. The subsequent procedure is as described in the May number. The method was used for fuel oils, kerosene, naphtha, coal, lignite, peat, etc.

The method described in the May number is an adaptation of the modified Henriques procedure for the determination of sulfur in rubber, which has been in use at the Bureau of Standards for several years. Goetzl's method differs from it in a few respects, one of which is believed to be of importance—that is the evaporation of the nitric acid, which may cause loss of a nitro-compound which carries sulfur.

The paper of Goetzl will be discussed in more detail in a future Technologic Paper of the Bureau of Standards.

BUREAU OF STANDARDS
WASHINGTON, D. C.
May 6, 1920

C. E. WATERS

COLLOIDAL FUEL

Editor of the Journal of Industrial and Engineering Chemistry:

Much to my astonishment and chagrin, the *New York Times* on April 16, in printing a report regarding the St. Louis meeting of the AMERICAN CHEMICAL SOCIETY, attributed to me the invention of the "colloidal fuel" described among other things in my paper on "Some Practical Applications of Colloid Chemistry."

The inventor is Mr. Lindon W. Bates, of New York, to whom I gave full credit in my paper.

As soon as I saw this erroneous report, I immediately telegraphed the *Times*, pointing out the error and requesting prompt publication of the truth, and the correction was made in their issue of April 17. Since some of my fellow chemists may have read the first report without seeing the second, I would ask you to do Mr. Bates and me the justice of publishing this letter.

RIDGEFIELD, CONN.
April 19, 1920

JEROME ALEXANDER

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[1] THIS JOURNAL, 11 (1919), 140.

[1] Goetzl, *Z. angew. Chem.*, **18** (1905), 1528.

MELTING POINT OF SODIUM NITRITE

Editor of the Journal of Industrial and Engineering Chemistry:

Several handbooks give the value of the melting point of sodium nitrite as 213° C.

E. Divers[1] gives the melting point as 271° C., a value which we have found to be substantially correct.

National Aniline & Chemical Co., Inc.
Buffalo, N. Y.
March 26, 1920

W. C. Gangloff

ENGINEERING DEGREES AT THE COLLEGE OF THE CITY OF NEW YORK

The Board of Trustees of the College of the City of New York has authorized the granting of degrees of Chemical, Civil, Electrical, and Mechanical Engineer on the satisfactory completion of a curriculum requiring five years. The announcement of the details of the curricula will shortly be issued. This is one of the steps taken by the College of the City of New York in the direction of closer coöperation between industry and colleges and universities.

PLATINUM THEFT

The University of Tennessee Agricultural Experiment Station, Knoxville, Tenn., on April 14, 1920, lost by theft 238.77 grams of platinum, in the form of eight dishes, Nos. 3, 5, 14, 16, 19, 20, 22, and 23, imprinted by dies. Two of the dishes weighed 22 and 23 grams, respectively, while the others weighed 31 to 32 grams each. $100 reward is offered for recovery.

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[1] *J. Chem. Soc.*, **75** (1899), 86.

NUMERICAL RELATION BETWEEN CELLS AND TREATMENTS IN EXTRACTION PROCESSES—CORRECTION

In the article of the above title [This Journal, 12 (1920), 493] there is a mistake in the arrangement of the tables on page 495, column 2. The first eight equations after the heading "Extractions in Which Every Charge Receives Two Treatments with Fresh Solvent" should appear in the footnote and only the last four equations should be in the body of the text. The correct footnote is as follows:

[1] The development of similar formulas for extractions in which every charge receives two treatments with fresh solvent (This Journal, *Loc. cit.*) will not be given in detail but following are the formulas for this method of extraction which have been developed by the same method as the foregoing:

Simultaneous Pumping

$$n = (3c - t)\,b + (3c - t - 1)\,p$$

$$a = 3b + 3p$$

$$e = b$$

Separate Pumping

$$n = bc\,(3c - t - 1) - (3c - t)\left(\frac{3c - t}{3} - 1\right)p \text{ when } t \text{ is multiple of 3}$$

$$n = bc\,(3c - t - 1) - \frac{(3c - t - 1)^2 - (3c - t - 1)}{3\,(3c - t)}\,p \text{ when } t \text{ is not multiple of 3}$$

$$a = 3b + (t + 2)\,p$$

$$e = b + (t/3 - 1)\,p \text{ when } t \text{ is multiple of 3}$$

$$e = b + \frac{(t - 1)^2 - (t - 1)}{3t^2}\,p, \text{ when } t \text{ is not multiple of 3}$$

Madison, Wisconsin

L. F. Hawley

WASHINGTON LETTER

By J. B. McDonnell, Union Trust Building, Washington, D. C.

Congress very probably will leave Washington without enacting any legislation at this session to protect the American dye industry. Brought up again on the floor of the Senate by Senator Watson, of Indiana, the dye bill ran up against a determined filibuster and after more than a week was put back on the calendar, where in all probability it will remain until Congress gets back to work following the conventions and campaign.

Failure of the dye bill—the strongest of the tariff measures passed by the House this session—to pass the Senate precludes the possibility of action on any of the other tariff measures pending in the Senate, including the Bacharach bill providing for the protection of the war-developed laboratory and scientific and surgical instruments and glassware. The bill for the protection of the potash industry, which began development in the United States during the war, has been forgotten in the House Ways and Means Committee.

The dye bill was brought up on May 1, following consideration of budget legislation by the Senate. The attitude of the opposition to the measure was shown as soon as the motion to take up the dye bill was made. Senator Moses, of New Hampshire, who perhaps has been the most bitter opponent of the measure, immediately made a point of no quorum, and Senator King, of Utah, Democrat, demanded a division on the vote on the motion, which, however, was carried easily.

As had been predicted, the dye bill had sufficient votes to pass it if it can be brought to a vote. It still has the required number of votes, although opponents have been working hard in the cloakrooms to convert supporters to their way of thinking. Support of the dye bill was voiced in a speech by Senator Frelinghuysen, of New Jersey, Republican, as soon as the bill was taken up. He supported the measure, the New Jersey Senator told the Senate, because of its importance to the national defense. He considered it second in importance only to the army and navy bills.

> Before the war, German interests, through partial or complete control of raw and semi-manufactured material, largely controlled the production of textiles, medical supplies, including aspirin and salvarsan and many other drugs in every-day use, electrical and automotive equipment, candy, chemicals, raw materials, and last but not least, coal-tar dyes, the key to the whole organic chemical industry.

Senator Frelinghuysen said:

> These industries and many others which I cannot at the present recall have passed into American hands. German patents filed in the United States are now controlled for America's needs and uses and secrets heretofore protected by laws against American competition are revealed to American manufacturers for the public benefit and profit.
>
> It is safe, therefore, to assume that with the passage of this bill the industrial influence which before the war Germany exercised in this country can never be restored.
>
> If Germany's industrial mailed fist extended across the seas and crushed this industry before the war and was prevented during the war, Germany's mailed fist is again appearing in opposition to this bill at the present time. I am told that agents in this country representing the German cartel, the powerful corporation that practically prevented the American industry from prospering before the war, are already conspiring and conniving and already have their lobby here in Washington to prevent the passage of this bill.

Quoting from a letter written by Thomas A. Edison, to Dr. Charles L. Parsons, in which Mr. Edison said that he had first manufactured aniline oil at the request of textile mills to prevent them from shutting down, Senator Frelinghuysen continued:

> I want to bear on that "to prevent the mills in this country from shutting down." I mention it to point out the selfishness of those textile industries in this country that are now opposing this measure. They have forgotten the great service rendered to them during the war when the supply of dyes and other products was cut off by reason of the war. They have forgotten that; and now, when they can get some of these raw materials and these dyes cheaper, they are indifferent to the interests of this great industry which was created during the war, and are opposing this legislation intended to protect and to retain that industry for America
>
> The story of the dye industry is one that shows the pitiful plight of a great country whose statesmen have lacked the vision to see that encouragement of industrial progress through the development of science was essential to the safety of the country and its people, who had placed their destiny in their hands.

Faced with a filibuster and threats to "talk the bill to death," supporters made little speech-making. Senator Thomas, of Colorado, Democrat, and declared opponent of every tariff measure reported from the Finance Committee, followed Senator Frelinghuysen. Senator Thomas began his speech of opposition on Monday, and held the floor until Saturday. Enactment of the dye bill would mean a monopoly, he declared, and quoted at considerable length from the statement made before the committee by John P. Wood, of Philadelphia, of the Piqua Mills.

Embodied in the Wood statement was the speech by Dr. Bernhard Hesse, and from this Senator Thomas quoted extensively to show conclusively that statements made by supporters as to the importance of the dye industry to the manufacture of explosives were not justified. He also criticized Dr. Charles H. Herty, who testified before the committee, declaring that "Dr. Herty has gone mad."

Senator Kenyon, of Iowa, Republican, opponent of the bill as reported from committee, interrupted Senator Thomas late in the week to read to the Senate a letter written by Charles K. Weston, of the publicity bureau of the du Pont Company, which Senator Kenyon said was an effort to intimidate Senator Moses. The letter simply stated that Mr. Weston had not been able to reconcile the position as regards the national defense taken in the Senate by Senator Moses, who opposed the dye bill, and the position he professed to take on the platform in support of the candidacy of General Leonard Wood, in whose campaign he was taking an active part as one of his managers. An accurate statement of his position was asked for in the letter, as Mr. Weston said he wished to be absolutely accurate in all statements made in a publicity campaign soon to be started to inform the public of the importance of the dye industry.

Following the reading of the letter a bitter tilt took place between Senators King and Frelinghuysen, the former launching a brief attack upon the New Jersey Senator which brought Senator Lodge, of Massachusetts, to his feet with a demand that the remarks be stricken from the record. After a long wait for a quorum, Senator King said that his remarks were susceptible of an interpretation he had not intended and withdrew them.

Consideration of the dye bill was interrupted technically but once, for a speech upon his peace resolution by Senator Knox, of Pennsylvania, although later in the week an afternoon was occupied in a debate on another matter.

Several efforts to work out a compromise measure for the selective importation section of the bill during its consideration met with failure and the Senate turned to other matters the following Monday, and on Tuesday, May 11, the dye bill was displaced from its favored position as the unfinished business of the Senate and put back on the calendar, where it is likely to remain for some time.

An attack upon the textile industry opponents of the dye bill was made by Senator Nugent, Democrat, of Idaho, who declared that the textile industry under Schedule K had received greater protection itself in the United States than any other industry.

Senator Moses has redrafted his proposed amendment to the bill, the most important features of the new revision probably being in a limitation upon imported dyestuffs of not more than a year's supply. Control of imports is removed from the Tariff Commission and placed under the Treasury Department. This amendment so far, however, has not found a response among supporters of the committee bill, and Democratic members are strongly opposed to it, although strongly in favor of the committee bill.

Contrary to plans, the Nolan bill providing for reorganization of the Patent Office, and increased compensation for the experts engaged there, which was passed by the House some time ago, has not come up for action in the Senate. This has been due largely to the fact that that body has been engaged in consideration of other matters which the leaders have determined to give the right of way.

St. John Perret, of the War Trade Board Section of the Department of State, who is in Europe in connection with American interests in the German and allied dyestuffs situation, is expected to return shortly.

No appropriation for continuing the work of the War Trade Board was granted by Congress and this will necessitate the closing of that board at the end of June, unless funds for carrying out the necessary work can be used from some lump sum appropriation given to the State Department. Apparently no one has yet made up his mind here as to just what the effect of this action by Congress will mean to the American chemical industry, inasmuch as the War Trade Board is charged with administering the import restrictions which still are in force under the wartime laws. Incidentally so long as this law is in effect, and the attitude of the executive branch of the Government does not change, the dye industry, of course, enjoys as much protection as it did during the war.

The dock strike at Amsterdam has ended and German dyestuffs which had been stored there awaiting shipment to this country have begun moving across the ocean.

Extension of its activities in experiments with helium gas is planned by the War Department, according to an announcement made recently, which stated that the helium gas experiment plant No. 2 (Army Air Service), at Petrolia, Texas, has been removed to Langley Field, at Hampton, Va. Plans for extending the work was the reason given for the transfer of the station.

Announcement of the production of potash in the United States during 1919, made by the United States Potash Producers Association, shows that the total output of potash salts was 119,736 short tons, or 32,418 short tons of K_2O, or actual potash. The average potash content of the salts produced was 27 per cent. This production is a decrease of approximately 40 per cent as compared with 1918 production, the Association states. Expected heavy imports resulted in lack of orders and forced plants to shut down or run on part time, so that the average operation was only six months, although some ran the entire year on part time.

Study of the use of narcotics will be made by a committee to be appointed by Secretary of the Treasury Houston. The actual work of carrying on the investigation will be under the direction of the surgeon general of the Public Health Service.

An important change made in the provisions of the Peace Treaty affecting the distribution and control of German dyestuffs became known here during the last month. Over the protests of representatives of the United States, a change was made under which Germany agrees to supply the allied and neutral countries with all intermediates and dyes needed for the next five years. This development is regarded here as extremely significant.

The proposal was put forward by the German government and is another attempt on the part of the German cartel to regain its foothold in the dye trade of the world, according to officials working for establishment of a dye industry in this country.

May 15, 1920

INDUSTRIAL NOTES

All German interests in the Alsatian Potash Works are being liquidated, and several financial groups, employing French capital exclusively, are being formed to acquire the interests. The former holders of shares have formed a new company with the object of securing if possible a direct or indirect interest in the potash works.

The Jordan Coal-Tar Products Company, Inc., of New York, has under construction at Matawan, N. J., a large plant occupying 10 acres of ground which will be operated to produce a full line of coal-tar products. James A. Dowd, vice president and general manager, who is in charge of the development, expects to have the plant in full operation by July 1.

The German Institute for Dye Research is being organized in Dresden with a branch at Chemnitz in the center of the German textile industry, under the direction of Professor Ostwald. The Institute is a national institution, supported by voluntary contributions from dye and textile industries, to maintain the superiority of German dyes. If the United States Congress passes the dye legislation, the Germans figure upon gaining American markets with their textile goods, while if this legislation is not passed they figure on gaining the American dye market.

The Calco Chemical Company has acquired the rights to the plant erected by them for the Government for the manufacture of tetranitraniline. This adjoins the Calco plant at Bound Brook, N. J., and consists of power plant, nitric and sulfuric acid plants, and buildings and equipment for the manufacture of dinitrobenzol, metanitraniline and tetranitraniline.

The Sloss-Sheffield Steel and Iron Company, of Birmingham, Ala., has recently put in operation sixty Semet-Solvay regenerative type ovens, each with a coking capacity of 2,500 tons of raw coal in 24 hrs., and sixty additional ovens are soon to be completed. Coke for furnace purposes with breeze screenings for boiler fuel will be produced, and tar will be marketed as a crude product. Ammonium distillates and light oil will be refined as toluene, benzene, and motor fuel. The plant is estimated to produce in 24 hrs. 1,800 tons of coke, 20,000 gal. of crude tar, 60,000 lbs. of ammonium sulfate, and 7,000 gal. of light oil.

The Continental Trading Company has recently been established in Tokio, Japan, with a capital of 10,000,000 yen, with the object of importing drugs, chemicals, surgical instruments, dyes, etc., from Germany and other countries.

The Trenton, Ontario, plant formerly owned by the British Chemicals, Ltd., and operated during the war by the Imperial Munitions Board, has been purchased by Chemical Products, Ltd., of Toronto. Fertilizers and pharmaceutical chemicals, including aspirin, will be produced after the necessary changes have been made.

The Association of Producers of Nitrate at Valparaiso has published statistics which show that in the month of February there was on hand in Europe a stock of nitrate of 150,000 tons and there were imported into Europe 237,000 tons. Of this total of 387,000 tons, 155,000 tons were delivered to the consumer, leaving 232,000 tons on hand for March. The world's total visible supply of nitrate is now 2,102,000 tons, located as follows:

	Tons
Chile	1,252,000
Europe	492,000
United States	277,000
Japan and other countries	81,000

Distribution of European nitrate imports during February, including 12,500 tons transshipped in the United Kingdom, was as follows:

	Tons
United Kingdom	11,000
France	90,000
Belgium	21,500
Holland	22,000
Spain and Portugal	18,000
Italy	39,000
Scandinavia	31,000
Egypt	7,500
Germany and Baltic ports	9,000

During the calendar year 1919 aniline dyes valued at $10,724,071 were exported from the United States. Japan was the greatest customer, then China, British India, and Canada. Following is a list of the larger countries to which the United States exported dyes and dyestuffs during 1919, and the values of the total shipments made:

	ANILINE DYES	LOGWOOD EXTRACT	ALL OTHERS
France	$ 127,059	$596,042	$ 229,689
Greece	51,530	7,100	19,257
Italy	269,130	58,716	180,359
Netherlands	26,284	21,735	9,104
Norway	13,663	1,300	7,303
Portugal	70,296	2,319	36,063
Russia	8,570	....	.....
Spain	535,383	18,349	84,544
Sweden	22,694	8,584	15,708
England	413,700	271,562	345,933
Canada	1,015,334	119,871	1,007,892
Mexico	467,806	17,438	230,359
Cuba	28,834	553	38,686
Argentina	468,459	8,552	186,798
Bolivia	25,444	186	333
Brazil	773,449	38,341	246,812
Chile	124,242	6,364	38,959
Colombia	35,247	2,176	23,691
Ecuador	31,530	615	9,149
Peru	136,813	6,595	34,440
Uruguay	42,747	2,075	35,210
Venezuela	13,909	1,117	7,835
China	1,609,060	370	519,283
British India	1,562,244	4,329	266,869
Dutch East Indies	137,265	68	12,347
French East Indies	48,168	....	11,141
Hong Kong	228,788	....	76,281
Japan	2,151,191	42,606	1,002,753
Australia	130,985	10,015	76,672
Philippine Islands	41,796	1,501	42,093
British South Africa	33,153	1,258	5,836

The Nitrogen Company of Providence, R. I., has purchased property in Providence where it plans to build a small plant for the manufacture of synthetic ammonia and other chemical products. Experiments have been carried on for some time at Niagara Falls, using hydrogen from the Mathieson Alkali Works, Inc. Details in regard to capitalization, officers, etc., of the Nitrogen Company have not yet been made public, but it is expected that the plant will begin operations within a few weeks.

The Rollin Chemical Corporation of Charleston, W. Va., suffered a $100,000 loss from a fire and explosion in the monochlorobenzene department on April 20. The cause of the explosion is not definitely known. Operation of the plant will continue during the work of rebuilding.

Included in the Department of Chemistry of the University of Kansas is the Division of State Chemical Research which has for its object the study of municipal or industrial problems of Kansas which lend themselves to chemical investigation. This Division has published a comprehensive chemical survey of the natural gases of Kansas and Oklahoma, of which the authors are Mr. H. C. Allen and Mr. E. E. Lyder.

The Southern Laboratory Supply Company has recently opened offices and a warehouse in Birmingham, Alabama, carrying a complete line of chemical, metallurgical and biological apparatus, scientific instruments, and chemicals.

The United States Civil Service Commission has announced an examination for assistant explosives chemist to fill a vacancy in the Bureau of Mines, Pittsburgh, Pa., and similar positions throughout the United States, at $2,400 to $3,000 a year. Competitors will be rated on education, experience, and publications, reports or thesis (to be filed with application). Applicants must have a Ph.D. degree, with major work in chemistry, or a bachelor's degree, together with subsequent work of research or technical character sufficient to be regarded as equivalent to a Ph.D. degree. Applicants must have had at least one year's experience in the analysis of explosives or explosives research. Applications must be filed with the Civil Service Commission, Washington, D. C., by June 22, 1920.

The United States Civil Service Commission has announced a competitive examination for chemical engineer, oil and lubrication research, at $3,000 to $4,000 a year. Vacancies in the Bureau of Standards, Washington, D. C., at $10 to $18 per diem when actually employed will also be filled from this examination. Competitors will be rated on education and training, experience, and publications and thesis (to be filed with application). Applications must be filed with Civil Service Commission, Washington, D. C., by June 22, 1920.

The United States Civil Service Commission announces an open competitive examination for food and drug inspector in the Bureau of Chemistry, at $1,600 a year. Candidates will be rated on the basis of answers to practical questions, a brief thesis to be written in the examination room, and education and experience. Applications should be filed with the Civil Service Commission, Washington, D. C., in time to arrange for the examination on June 9, 1920.

The United States Civil Service Commission announces an examination for assistant for fishery food laboratory to fill a vacancy in the Bureau of Fisheries, Department of Commerce, Washington, D. C., at $2,000 to $2,400 a year. Applicants will be rated on experience and education, and upon a thesis to be filed with the application. Applications must be filed with the Civil Service Commission, Washington, D. C., by June 22, 1920.

The New Jersey Fish and Game Commission has charged the chemical plants along the Delaware River with polluting the water by wastes, thus driving away the fish and killing the spawn. The Commission believes that the sewage could be filtered at a small expense. Experts of the State Department of Health are to investigate the matter.

The Farmers' Coöperative Phosphate and Fertilizer Company has been organized in Mulberry, Florida, with $5,000,000 capital, and has purchased 3,700 acres of phosphate land estimated to contain nearly 10,000,000 tons of pebble phosphate rock averaging 65 to 75 per cent bone phosphate of lime. Additional lands estimated to contain from 4,000,000 to 5,000,000 tons have been contracted for. A phosphate plant located on the first tract is being improved to give an annual mining output of 50,000 tons, and an additional plant with a capacity of 200,000 tons is planned.

The California Fruit Growers Exchange, an organization of 10,000 growers of citrus fruits, has established a research laboratory in Corona, California, in charge of Mr. C. P. Wilson, who was for thirteen years with the Bureau of Chemistry of the U. S. Department of Agriculture. The purpose of the new laboratory is to work out new products from all varieties of citrus fruits. The first work will be in connection with the utilization of the lower grades of fruit as by-products. Both the lemon growers and the orange growers of the Exchange have organized by-products companies, each with its own plant control laboratory, with which the research laboratory will coöperate.

The Committee on Food and Nutrition of the National Research Council has issued a report on meat and milk in the food supply of the nation, giving interesting facts on their relative values in the national dietary. It is estimated that about 18 per cent of the energy of grain used in feeding the animal is recovered for human consumption in milk, but only about 3.5 per cent is recovered in beef. Similarly it has been estimated that the crops grown on a given area will yield from four to five times as much protein and energy when fed to dairy cows as when used for beef production. In providing mineral elements and vitamines the milch cow contrasts even more favorably with the beef animal. The vitamines and calcium furnished by hay and grain are stored in the tissues only to a slight extent, but are furnished in relative abundance in the milk.

During 1919 the chemical industry in Japan spent more money in the extension of its works than any other industry. Forty-seven factories were enlarged and 33,957,000 yen were added to the authorized capital of chemical companies. Of the 213 manufacturing companies which went out of business during the year, 57 were chemical works with total capitalization 26,638,000 yen.

PERSONAL NOTES

Mr. Louis W. Mahle has severed his connections with the Barrett Co., Frankford, Philadelphia, Pa., to accept the position of chemical engineer with the Ohio Boxboard Co., Rittman, Ohio.

Dr. Van H. Manning, director of the Bureau of Mines, Department of the Interior, tendered his resignation, effective June 1, to President Wilson. Dr. Manning is leaving the government service to accept a position as director of research with the recently organized American Petroleum Institute, the most important body of petroleum men of the country. Dr. Manning is to be succeeded by **Dr. Frederick G. Cottrell**, of California, who was nominated by President Wilson on May 5 to be director of the Bureau of Mines.

Mr. I. Frank Stone, one of the leading manufacturing chemists in the country and a former president of the National Aniline & Chemical Co., died May 5. Mr. Stone was a member of the American Chemical Society since 1904, and was president of the Chemists' Club in 1920.

Mr. John Wesley Hyatt, noted inventor, died recently at his home at Short Hills, N. J., at the age of eighty-three. In 1914 the Society of Chemical Industry conferred upon Mr. Hyatt the Perkin Medal for his distinguished services in the field of applied chemistry and engineering.

Mr. Oliver Sheppard Picher, president of the Eagle-Picher Lead Co., died on April 26 after a short illness of pneumonia, at his home in Winnetka, Illinois.

Mr. Robert G. Dort is now with the Bregeat Corporation of America, a subsidiary of the International Coal Products Corporation, Newark, N. J., on publicity and sales work concerning a solvent recovery process which was used in France and England during the war.

Mr. Sidney M. Hull resigned last February from his position as assistant superintendent of the Norwood Dye Works of the Ault & Wiborg Co., Cincinnati, Ohio, to accept a place in the laboratory of the Newport Co., Carrollville, Wis., as research chemist on basic intermediates.

Mr. H. D. Corkum has left the Sayles Finishing Plants, Saylesville, R. I., where he was employed as superintendent of the worsted department, and has taken a technical position with the du Pont Dyestuff Sales Department, Wilmington, Delaware.

Mr. Chandler T. White, formerly chemist at the Winchester Repeating Arms Co., New Haven, Conn., is at present in the research laboratory of the New Jersey Dye Works of the Grasselli Chemical Company.

Mr. A. M. Allison of Brookings, S. D., senior student research assistant in the department of chemistry at State College, has received an appointment to a research assistantship in organic chemistry at Northwestern University, Evanston, Illinois.

Mr. F. C. Shotwell, formerly instructor in chemistry, Easton High School, Easton, Pa., has been made principal of the high school at Woodbridge, New Jersey.

Mr. Henry Howard has severed his connection with the Merrimac Chemical Co., North Woburn, Mass., and is associated with the Grasselli Chemical Co., Cleveland, Ohio.

Mr. W. H. Matthews, for a short time with the F. S. Royster Guano Co., Baltimore, Md., is now with the Liberty Yeast Corporation as superintendent of their plant at Cambridge, Mass.

Mr. Oliver Loud, formerly plant chemist of the citrus by-products factory of the California Fruit Growers Exchange, at Corona, Cal., and during the latter months of the war assistant in physiological research with the Chemical Warfare Service, is now engaged as chemist at the Richmond, Cal., refinery of the Standard Oil Co. of California.

Mr. S. R. Scholes has resigned as chemist for H. C. Fry Glass Co., to become general manager of the newly organized Utility Glass Works, Lonaconing, Maryland.

Dr. James Brown, formerly research chemist for Zinsser and Co., Hastings-on-Hudson, N. Y., has accepted a similar position with the Calco Chemical Co., Bound Brook, New Jersey.

Mr. A. M. Muckenfuss resigned as professor of organic and industrial chemistry and director of that sub-department, Emory University, Atlanta, Ga., to go with the Roessler & Hasslacher Chemical Co., Perth Amboy, N. J., as research chemist.

Mr. A. U. Stjernlof resigned as assistant chemist in the Brooklyn Navy Yard to take new duties with the American Agricultural Chemical Co., at Carteret, New Jersey.

Mr. H. P. Fishburn, formerly with the University of Idaho, is now chief chemist for the Standard Oil Co. of Indiana, at their works at Casper, Wyoming.

Mr. Conrad E. Thies has severed his connections with the Palo Company, and has associated himself as vice president with the Rohde Laboratory Supply Co., New York City.

Mr. A. H. Mitchell, formerly chemist for the Warner Iron Co., Nashville, Tenn., and later chemist for the Bonair Coal & Iron Corp., of the same city, is now furnace chemist for the Suwanee Iron Co., of Nashville.

Dr. N. R. Blatherwick, who has been in the employ of the U. S. Department of Agriculture as physiological chemist in the Dairy Division, Bureau of Animal Industry, has become biochemist of the Memorial Laboratory Clinic, at Santa Barbara, California.

Dr. Harry N. Holmes, head of the chemistry department, Oberlin College, is giving a series of lectures on the "Chemistry of Colloids." The places visited include the Universities of California, Washington, and Wisconsin, Northwestern University, Leland Stanford University, State College of Washington, Montana School of Mines, State Colleges of Montana, North Dakota and Iowa, also the Los Angeles, San Francisco and Seattle Sections of the American Chemical Society.

Mr. L. B. Schofield, formerly with the Huntington Chemical Co., Huntington, Ind., is assistant in the research department of the Commonwealth Edison Co., Chicago, Illinois.

Mr. J. C. Blucher left the employ of American Smelting and Refining Co., Tacoma, Wash., to assume office work in the employ of the Seattle Chain Company.

Mr. George B. Frankforter, formerly examiner of explosives, chemicals and loading in the Ordnance Claims Board and later technical adviser to the War Claims Board, returned recently to the University of Minnesota as professor of organic and industrial organic chemistry.

Dr. Arthur W. Dox has resigned as chief in chemistry of the Iowa Agricultural Experiment Station to accept the position of research chemist for Parke, Davis & Co., Detroit, Michigan.

Dr. Charles L. Parsons, secretary of the American Chemical Society, sailed recently for Europe. Dr. Parsons will visit several of the most important chemical centers of the continent and will attend the International Union of Pure and Applied Chemstry in Rome.

Mr. Edwards F. Wilson, for a number of years chief chemist of the Westmoreland Coal Co., prior to which time he was chemist for Woodward Iron Co., Ala., and chief chemist of the Virginia Iron, Coal & Coke Co., and also in charge of the Iron-Masters' Laboratory of Philadelphia, is opening an independent commercial testing laboratory and consulting office in Philadelphia.

Mr. F. A. Burningham, formerly with the U. S. Bureau of Mines, Pittsburgh, Pa., is at present employed as research chemist in the research department of Brown Co., Berlin, New Hampshire.

Dr. William H. Walker recently resigned as director of the research laboratory of applied chemistry of the Massachusetts Institute of Technology because of the pressure of duties in connection with his position as director of the division of industrial coöperation and research, and **Prof. Robert E. Wilson**, formerly assistant director, was appointed to the position of director. In view of the enlarged scope of the laboratory work, two assistant directors have been appointed, **Dr. C. S. Venable**, in charge of organic problems, and **Dr. L. W. Parsons**, in charge of inorganic problems.

Dr. C. E. K. Mees, director of the research laboratories of Eastman Kodak Co., Rochester, N. Y., while in England will deliver before various scientific bodies lectures on various aspects of photography and on the general subject of industrial research.

Mr. Thomas J. Keenan has resigned as editor of *Paper*, and is now located at 18 East 41st Street, New York City, where he will devote his entire time to his work as secretary-treasurer of the Technical Association of the Pulp and Paper Industry.

Mr. Eugene F. Hickson has resigned from the paint section of the Bureau of Standards to go in the research department of the American Writing Paper Co., Holyoke, Massachusetts.

Mr. J. M. Krauss, previously employed as first assistant chemist for the New York & Pennsylvania Co., paper makers, has accepted the position of chief chemist for the District of Columbia Paper Manufacturing Co., Washington, D. C.

Mr. Chas. H. Plantz has left the engineering department of the Edison Lamp Works, Harrison, N. J., and is now connected with the St. Regis Paper Co., Deferiets, N. Y., as chemist.

It was recently announced that **Dr. Ira Remsen**, of Johns Hopkins University, Baltimore, Md., will deliver the commencement address at West Virginia University, Morgantown, W. Va., on June 15.

Dr. W. D. Bancroft, of Cornell University, **Dr. E. P. Kohler**, of Harvard University, and **Dr. E. V. McCollum**, of Johns Hopkins University, have recently been elected members of the National Academy of Sciences. **Dr. Arthur L. Day**, of the Geophysical Laboratory, Washington, D. C., is a newly elected member of the Council of the above Academy.

The Franklin Medal of the Franklin Institute, Philadelphia, Pa., was awarded May 19 to **Prof. Svante August Arrhenius**, Nobel Institute, Stockholm, Sweden. In connection with the presentation of the above medal **Dr. Allerton S. Cushman**, director of the Institute of Industrial Research, Washington, D. C., read a paper by Professor Arrhenius entitled "The World's Energy Supply."

Mr. Lucien H. Greathouse resigned as assistant chemist at the Fixed Nitrogen Research Laboratory, War Department, recently, to accept a position in experimental work with the Atmospheric Nitrogen Corp., Laurel Hill, N. Y.

Dr. Raymond F. Bacon, director of the Mellon Institute of Industrial Research, who, during 1918, was a Colonel in the Chemical Warfare Service, serving as chief of the Technical Division of the Chemical Warfare Service, A. E. F., has been awarded a citation by General Pershing for exceptionally meritorious and conspicuous services in France.

Mr. C. J. Haines, formerly in charge of manufacturing operations at the Chicago, Ill., refinery of the American Cotton Oil Co., has become superintendent of the Electrox Co., Peoria, Illinois.

Mr. Klare S. Markley resigned his position with the Department of Agriculture to accept one as chemical engineer with the Valley Mould & Iron Corporation, at their Sharpsville, Pa., plant, where he will undertake research on cast ingot molds as made in the direct pouring process.

GOVERNMENT PUBLICATIONS

By Nellie A. Parkinson, Bureau of Chemistry, Washington, D. C.

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

CONGRESSIONAL COMMITTEES

Coal-Tar Products. Importation of coal-tar products, views of minority to accompany House Report 8078 (to regulate importation of coal-tar products, to promote the establishment of manufacture thereof in United States, and to amend act of September 8, 1916, to increase revenue, and for other purposes); submitted by Mr. Moore of Pennsylvania. House Report 209, Part II. 8 pp. 1920.

Glass. Duty on laboratory glassware and surgical and scientific instruments, report to accompany House Report 7785 (to provide revenue for Government, to establish and maintain in United States manufacture of laboratory glassware, laboratory porcelain ware, optical glass, scientific and surgical instruments); submitted by Mr. Curtis. Senate Report 459. 4 pp. March 2, 1920.

Magnesite. Duty on magnesite ores, report to accompany House Report 5218 (to provide revenue for Government and to establish and maintain production of magnesite ores and manufactures thereof in United States); submitted by Mr. Curtis. Senate Report 458. 3 pp. March 2, 1920.

Tungsten Ores. Report to accompany House Report 4437 (to provide revenue for Government and to promote production of tungsten ores and manufactures thereof in United States); submitted by Mr. Curtis. Senate Report 487. 2 pp. March 23, 1920.

Paper. Distribution and consumption of print paper in the United States, report in response to resolution regarding supply, distribution, and consumption of print paper in the United States. House Document 696. 24 pp. March 22, 1920.

UNITED STATES TARIFF COMMISSION

Dyes and Dyeing. Costs of production in dye industry, July 1918 to September 1919, details of costs for selected list of dyes and intermediates. Tariff Information Series 15. 24 pp. 1920.

INTERIOR DEPARTMENT

Petroleum. Regulations concerning oil and gas permits and leases (including relief measures) and rights of way for oil and gas pipe lines, authorized by act of February 25, 1920 (Public 146); approved March 11, 1920. Circular 672. 38 pp. Paper, 5 cents. 1920.

UNITED STATES PUBLIC HEALTH SERVICE

The Importance of Tellurium as a Health Hazard in Industry—A Preliminary Report. M. D. Shie and F. E. Deeds. Public Health Reports, **35**, 939–54 (April 16, 1920).

Ozone in Ventilation. Some Abstracts from the Literature on the Use of Ozone in Ventilation. Public Health Reports, **35**, 989–93 (April 23, 1920).

GEOLOGICAL SURVEY

The Sunset-Midway Oil Field, California. R. W. Pack. Geology and Oil Resources. Part I. 179 pp. 1920. The report describes the general geology of the Sunset-Midway region, the development and underground conditions in the productive field, and also the origin and migration of the oil.

The Work on Mineral Resources Done by the United States Geological Survey. E. S. Bastin and H. D. McCaskey Separate from Mineral Resources of the United States, 1918. Part I. 5 pp. Issued March 31, 1920. A resumé of the development and scope of this work is given.

Zinc in 1917. C. E. Siebenthal. Separate from Mineral Resources of the United States, 1917. Part I. 25 pp. Issued April 6, 1920. The following table is given showing the amount of zinc produced and consumed in the United States, 1911–1917, in short tons.

Zinc Produced and Consumed in the United States, 1911–1917, in Short Tons

	1911	1912	1913	1914	1915	1916	1917
Production of primary zinc:[1]							
From domestic ore	271,621	323,907	337,252	343,418	458,135	563,451	584,597
From foreign ore.	14,905	14,899	9,424	9,631	31,384	104,005	84,976
	286,526	338,806	346,676	353,049	489,519	667,456	669,573
Production of secondary zinc:[1]							
Redistilled.......	14,043	26,064	25,991	20,545	29,764	29,663	16,835
Remelted........	26,470	26,187	24,014	22,424	23,136	21,037	14,565
	327,039	391,057	396,681	396,018	542,419	718,156	700,973
Apparent consumption of primary zinc............	280,059	340,341	295,370	299,125	364,632	458,428	413,643

[1] "Primary zinc," which is produced directly from ore, is here distinguished from "secondary zinc," which is obtained by refining zinc ashes, skimmings, drosses, and old metals. The statistics of secondary zinc are given on page 860. Wherever in this report the word "zinc" is used without qualification it means primary zinc.

This is an increase of 21,146 tons, or about 4 per cent, in quantity, and a decrease of $31,747,000, or about 21 per cent, in value, as compared with similar figures for 1916.

Potash in 1918. W. B. HICKS. Separate from Mineral Resources of the United States, 1918. Part II. 61 pp. Issued March 31, 1920. This report differs from previous annual reports on potash in that it deals not only with potash materials derived from original sources, but with refined potassium salts as well. The production of potash-bearing materials in 1918 was nearly 70 per cent more than in 1917, and represented about 22 per cent of the normal consumption in the country, which is estimated to be 25,000 short tons annually. The following table shows the increase in the domestic production of potash during the last few years and gives some idea of the growth of the industry:

POTASH PRODUCED AND SOLD IN THE UNITED STATES, 1915–1918

	Number of Producers		Production		Sales[1]		
YEAR	Total	Exclusive of Producers of Wood Ash Potash	Crude Potash (Short Tons)	Available Content of Potash (K_2O) (Short Tons)	Crude Potash (Short Tons)	Available Content of Potash (K_2O) (Short Tons)	Value f. o. b. Plant
1915	5[2]	5	4,374	1,090	4,374	1,090	$342,000
1916	70	25	35,739	9,720	35,739	9,720	4,242,730
1917	95	46	126,961	32,573	126,961	32,573	13,980,577
1918	128	77	207,686	54,803	140,343	38,580	15,839,618

[1] Production and sales were practically the same from 1915 to 1917, and no distinction was made between them.

[2] Although no production was reported from wood ashes it is probable that an appreciable quantity of potash was produced from that source in 1915.

In 1918 the production came from 10 distinct classes of raw materials. Natural brines furnished about 73 per cent of the output, the Nebraska lakes alone contributing about 53 per cent and Searles Lake, Cal., the second largest quantity from a single source. Kelp yielded about 9 per cent of the total production, followed by smaller contributions from molasses, alunite, cement, etc.

The domestic production of refined potassium salts in 1918, exclusive of chlorides and sulfates, amounted to 53,661,676 lbs., and the sales amounted to 43,833,503 lbs., valued at $16,032,880.

Asphalt and Allied Substances in 1918. C. C. OSBORN. Separate from Mineral Resources of the United States, 1918. Part II. 58 pp. Issued March 31, 1920. The quantity of asphalt and allied substances produced in the United States in 1918 was 1,237,853 short tons, valued at $18,540,032, a decrease of about 13 per cent in output, but an increase of a little more than 16 per cent in value, compared with similar figures for 1917. The report shows that the output and value of asphalt and allied substances have materially increased in recent years.

Strontium in 1918. G. W. STOSE. Separate from Mineral Resources of the United States, 1918. Part II. 4 pp. Published March 30, 1920. The strontium industry in the United States seems to have reached its climax in 1918. The following table permits comparison with the production of previous years:

CRUDE STRONTIUM ORES MINED AND SOLD IN THE UNITED STATES, 1916–1918, IN SHORT TONS

MINERAL	1916	1917	1918
Celestite	240	3,630	0
Strontianite	10	405	400

Talc and Soapstone in 1918. J. S. DILLER. Separate from Mineral Resources of the United States, 1918. Part II. 7 pp. Issued March 29, 1920. The production of talc has increased somewhat over pre-war years. Nearly 4 per cent less domestic talc was sold in 1918 than in 1917, but because of the advance in price the value was about 11 per cent greater. The total production of soapstone in the United States in 1918 was 16,830 short tons, valued at $591,059. No imports of soapstone into, or exports from, the United States are reported.

Cement in 1918. E. F. BURCHARD. With Sections on Imports and Exports in Foreign Countries, R. S. SCHULTZ, JR. With Sections on Concrete Ships, R. W. LESLEY. Separate from Mineral Resources of the United States in 1918. Part II. 39 pp. Issued April 9, 1920. The marked decline in the output of cement in 1918, amounting to about 22 per cent as compared with 1917, was the result of the continued curtailment begun in 1917 of building operations not essential to the war and of the continuation of the war restrictions imposed by the Government upon fuel supplies, transportation facilities, and labor. The output in 1918 was the lowest since 1909. On the other hand, wages and fuel costs continued to increase to such an extent that selling prices of cement were advanced greatly, that of Portland cement reaching an average of nearly $1.60 a barrel at the mills, the highest price in 20 years.

Secondary Metals in 1918. J. P. DUNLOP. Separate from Mineral Resources of the United States, 1918. Part I. 21 pp. Issued April 9, 1920. Dealers in and refiners and smelters of scrap metals and drosses continued to do a large business up to November 1918, but the business done was not so profitable or so large as in 1916 and 1917. During the last two months of 1918 business was stagnant and the value of stocks decreased considerably. The following table shows the secondary metals recovered in the United States in 1917 and 1918:

SECONDARY METALS RECOVERED IN THE UNITED STATES IN 1917 AND 1918

	1917		1918	
	Quantity (Short Tons)	Value	Quantity (Short Tons)	Value
Secondary copper, including that in alloys other than brass	159,400	$87,032,400	122,510	$60,519,900
Remelted brass	320,000	141,888,000	328,800	128,696,300
Secondary lead	45,100	16,082,000	41,146	13,788,200
Recovered lead in alloys	48,400		55,954	
Secondary zinc	31,400	7,384,800	27,108	6,950,600
Recovered zinc in alloys other than brass	4,800		11,082	
Secondary tin	6,000	23,920,200	7,142	41,381,000
Recovered tin in alloys	13,400		16,695	
Secondary antimony	6	2,061,700	43	1,317,000
Recovered antimony in alloys	4,955		5,183	
Secondary aluminum	6,660	16,711,800	6,050	10,113,600
Recovered aluminum in alloys	9,440		9,000	
Secondary nickel[1]	60	774,000	178	1,532,300
Recovered nickel in alloys[1]	800		1,215	
	...	295,854,900	...	264,298,900

[1] Recoveries made by International Nickel Company from scrap nickel or alloys and from nickel in scrap ferrous alloys from any source are not included.

Iron Ore, Pig Iron, and Steel in 1918. E. F. BURCHARD. Separate from Mineral Resources of the United States, 1918. Part I. 58 pp. Issued April 20, 1920. The year 1918 was characterized in the American iron and steel industry by almost complete devotion to the needs of the Government for war purposes. The period shows a great contrast between the unsatisfied demand and fixed prices at the beginning of the year and the low demand and decreased prices due to the cessation of hostilities and the hesitancy of the normal market at the end of the war.

Manganese and Manganiferous Ores in 1918. D. F. HEWETT. Separate from Mineral Resources of the United States, 1918, Part I. 50 pp. Issued April 10, 1920. In 1918 domestic shipments of high-grade ore were more than twice those of 1917, nearly ten times those of 1916, and more than 30 times those of 1915. The rate of production of ore attained the maximum during the third quarter of the year, but after the armistice was signed it decreased rapidly. The imports of ore were 491,303 tons, or 138,669 tons less than in 1917. Imports of ferromanganese in 1918 were 27,168 tons, compared with 41,969 tons in 1917, and were the lowest since 1904.

BUREAU OF MINES

Monthly Statement of Coal-Mine Fatalities in the United States, January 1920. W. W. ADAMS. 7 pp. Paper, 5 cents. March 1920.

Blowholes, Porosity, and Unsoundness in Aluminum-Alloy Castings. R. J. ANDERSON. 34 pp. Paper, 10 cents. December 1919.

Approved Explosion-Proof Coal-Cutting Equipment. L. C. ILSLEY AND E. J. GLEIM. Bulletin 78. 53 pp. Paper, 25 cents. 1920.

BUREAU OF STANDARDS

Recommended Specifications for Red Lead, Dry and Paste. Circular 90. 8 pp. Issued April 3, 1920. Prepared and recommended by the United States Interdepartmental Committee on Paint Specification Standardization, January 26, 1920. Outlines specifications for the dry pigment and paste, methods of sampling and analysis, and describes the reagents to be used in examining these products.

Recommended Specification for Ocher, Dry and Paste. Circular 91. 8 pp. Issued April 15, 1920. Prepared and recommended by the United States Interdepartmental Committee on Paint Specification Standardization, March 22, 1920.

Ocher may be required in the form of dry pigment or paste ground in linseed oil; it shall be prepared in accordance with the most improved methods. Grinding in oil shall be thorough and the vehicle shall be pure raw linseed oil.

The material shall be bought by net weight.

(*a*) DRY PIGMENT—The pigment shall be a hydrated oxide of iron permeating a siliceous base, and shall be free from added impurities. It shall conform to the following requirements:

Color—Color Strength—Tone—Equal to sample mutually agreed on by buyer and seller.

	Maximum Per cent	Minimum Per cent
Coarse particles: Retained on standard No. 200 screen[1]	0.0	..
Iron oxide	...	17
Lime (CaO)	5	..
Lead chromate	None	..
Organic colors	None	..

[1] No. 200 screen is the same as screen formerly known as 200 mesh.

(*b*) PASTE—Ocher in paste form shall consist of:

	Maximum Per cent	Minimum Per cent
Pigment	71	69
Linseed oil	31	29
Moisture and volatile matter	0.5	..
Coarse particles and "skins" (total residue left on No. 200 screen) based on pigment	0.5	..

Turbidity Standard of Water Analysis. P. V. WELLS. Scientific Paper 367. 29 pp. Paper, 10 cents. Issued March 17, 1920. The study of the present standard of turbidity in water analysis has shown it to be inaccurate, the variations from the average in some cases amounting to over 50 per cent. This could be eliminated largely by having all the standards prepared by the Bureau of Standards. There seems to be no reason why the standard should not be made precise to at least 10 per cent. There is a possibility that standard samples of dry powdered silica can be prepared sufficiently uniform in size of particle to use directly.

Vapor Pressure of Ammonia. C. S. CRAGOE, C. H. MEYERS AND C. S. TAYLOR. Scientific Paper 369. 35 pp. Paper, 10 cents. Issued April 10, 1920.

A New Cadmium-Vapor Arc Lamp. FREDERICK BATES. Scientific Paper 371. 6 pp. Paper, 5 cents. Issued April 10, 1920.

Investigation of the Compressive Strength of Spruce Struts of Rectangular Cross Section and the Derivation of Formulas Suitable for Use in Airplane Design. J. E. BOYD. Technologic Paper 152. 43 pp. Paper, 10 cents. Issued April 10, 1920.

A Peculiar Type of Intercrystalline Brittleness of Copper. H. S. RAWDON AND S. C. LANGDON. Technologic Paper 158. 5 pp. Paper, 5 cents. Issued April 10, 1920. Describes the behavior of copper when heated in a molten salt bath (sodium chloride).

DEPARTMENT OF AGRICULTURE

Crop Injury by Borax in Fertilizers. OSWALD SCHREINER, B. E. BROWN, J. J. SKINNER AND M. SHAPOVALOV. Department Circular 84. 35 pp. Paper, 10 cents.

A Machine for Trimming Camphor Trees. G. A. RUSSELL. Department Circular 78. 8 pp. Paper, 5 cents. Issued February 1920.

COMMERCE REPORTS—APRIL 1920

The French office of Controller General of Spirits and Combustibles has been discontinued and the work of that department placed under the control of the Ministry of Public Works. (P. 3)

Statistics of exports of **beeswax** and **graphite** from Madagascar to the United States are given. (P. 5)

Large bedded deposits of good quality **magnesite** are reported to exist in South Manchuria, China, close to a trunk-line railroad. (P. 26)

It is estimated that an annual production of 2,500 tons of **asbestos** can be obtained in North China after production is stimulated by fair prices. (P. 26)

Outside capital is being sought for the development of a number of **asbestos** and **tungsten** mines in China. It is said that if Americans do not evince an interest the holders of concessions will have to turn to the Japanese for assistance. (P. 26)

A **paper-manufacturing** plant was established in Tunis during January 1920. It is equipped with modern machinery and will have a daily output of about 3,000 kilos of paper. (P. 29)

The outstanding feature of the **leather** situation in France is the present shortage of the better grades of upper leather, coupled with a surplus of certain classes of raw hides and calfskins, which, on account of insufficient tanning facilities, cannot be worked up in the country. The expansion of the domestic tanning facilities is restricted by a shortage of labor and chemicals and difficulties of transport. Sole leather is produced in slight excess of domestic consumption. Tanned sheepskins and kid and lamb gloves constitute the only important leather exports. (Pp. 33–5)

A company has been formed in India to manufacture toys, **glassware**, etc., from tin, wood, rubber, metal, wax, aluminum, and leather. (P. 36)

The **imports** from the United States into Spain of coal and petroleum residues, iron, steel and other metallic products, and chemical products, especially dyes, paints, soda, and paraffin, have greatly increased since the war. (Pp. 67–73)

A market for **glassware** in Malta is reported. (P. 121)

By an order in council, dated November 22, 1919, the importation of the following **dyestuffs** into Nigeria is prohibited:

(*a*) All derivatives of coal tar generally known as intermediate products capable of being used, or adapted for use, as dyestuffs, or of being modified or further manufactured into dyestuffs.

(*b*) All direct cotton colors, all union colors, all acid colors, all chrome and mordant colors, all alizarin colors, all basic colors, all sulfide colors, all vat colors (including synthetic indigo), all oil spirit and wax colors, all lake colors, and any other synthetic colors, dyes, stains, color acids, color lakes, leuco acids, leuco basis, whether in paste, powder, solution, or other form.

This order does not extend to dyestuffs which are the produce or manufacture of any part of the British Empire, or are imported in accordance with the terms of any license issued by the comptroller. (P. 126)

Secretary of Commerce Alexander recommends the saving of all **waste paper**. (P. 131)

There has been a great increase in the traffic in **ginseng** in Hongkong as a result of the ending of the war and the gradual return to more normal trade. (P. 147)

A shortage of **paint** and **linseed oil** in New Zealand is reported. (Pp. 150–1)

Statistics are given showing the quantity and value of **potash compounds** shipped into Great Britain from Germany and Alsace for agricultural and industrial purposes since the armistice. (Pp. 156–7)

It is reported that an American concern is actively engaged in the development of Chinese **mining** property. (P. 158)

It is reported that a Chinese merchant desires to sell to American buyers the output of a Chinese **mica** deposit. (P. 158)

The development of the **kauri gum industry** in New Zealand is reviewed. (Pp. 160–1)

The British committee which was sent to Germany to investigate the **dyestuff** situation reports that it found the stocks of dyestuffs available in Germany to be very small indeed. Very little, if any, manufacturing of dyestuffs was being carried on. Only by some concerted and well-organized effort, says the committee, can the British dye users expect to obtain in the future such stocks of European dyes as will enable them to meet all their requirements. (P. 167)

The Commonwealth Flax Industry Committee, which was established by the Australian government on the recommendation of the Institute of Science and Industry, has recommended the government to continue the guaranty for **raw flax**. It is understood that the government does not intend to let this industry languish. (Pp. 169–71)

It is reported that many of the large German **chemical** plants have had to close down on account of the coal shortage. (P. 173)

The German **potash** industry lacks coal and cars and the exports and domestic consumption of potash declined in February, notwithstanding the fact that they received a larger amount of fuel than in the previous month. (P. 173)

A company has been formed for the exploitation of **phosphate** in Tunisia with a capital of 16,000,000 francs. (P. 182)

Switzerland does a very fair trade in both imports and exports of **asbestos**. (P. 183)

The **oil-bearing seeds** and **nuts** and other oil-yielding material produced in Burma include, in the order of their importance, peanuts, sesamum, and cottonseed. (Pp. 184–6)

Swedish importations of **petroleum** products were heavy during the latter part of 1918 and the whole of 1919. Most of these products are imported from the United States, but Great Britain appears to be increasing its share of the trade in vaseline. (P. 195)

The present production of **borax** in Asia Minor is less than before the war, largely owing to labor shortage. (Pp. 210–1)

The **oil-bearing seeds** and **nuts** and their products in North Manchuria are reviewed. The only oil-bearing materials produced in commercial quantities are soy beans and hempseed. (Pp. 212–7)

Although the production of **tar** still plays its part in Finnish industrial life, it has now become quite insignificant compared with its importance 50 years ago. (Pp. 217–20)

The average annual production of **sesame seed** in Mexico is 80,000 tons, practically the whole crops being consumed in Mexico, since local prices are higher than those offered by foreign buyers. (P. 227)

The various branches of the Swedish **technical chemical industry** showed development during the war in proportion to their freedom from dependence upon raw materials from abroad. Sweden affords a market for colors, paints, and varnishes. (P. 228)

The Mexican wells now under exploitation are capable of producing 170,000 cubic meters of **petroleum** per day, or approximately 1,000,000 bbls. (Pp. 245–6)

A marked decrease is noted in the imports from Germany to France of **chemical products** during the year 1919. (Pp. 257–62)

Statistics are given showing the distribution of **lime** in the different German industries during the month of March 1920. (P. 275)

It is almost useless for American manufacturers and importers to visit Belgium or conduct negotiations in the hope of obtaining shipments of **plate glass**. The syndicate of plate glass manufacturers is overwhelmed with domestic and export orders, including several from the United States, which cannot be filled under present conditions. (Pp. 276–7)

The export of **cassia** out of Hongkong in 1919 assumed prewar proportions. On the whole, the trade was quite satisfactory, although it was more or less irregular, inasmuch as nearly half of the total exports were shipped in the third quarter of the year. The declared exports of cassia oil to the United States in 1919 were valued at $288,836, as compared with $124,465 in 1918. (P. 284)

Window-glass production in Belgium has probably been more completely revived than any important Belgian industry. All factories are booked well ahead with orders, however, and there is not much probability of greatly increasing production under present conditions. (P. 289)

There is reported to be a market in Palestine for American **caustic soda, drugs** and **patent medicines, leather, oleo oil, coconut oil, margarine,** and **paper.** (P. 291)

The **mineral** production of Canada shows a decrease in 1919 as compared with 1917 and 1918. Gold was the only metal of which there was an increased production during 1919. (Pp. 300–3

There was no production of **manganese** in the Caucasus in 1918 and 1919. (P. 321)

Since the milling of **copra** was commenced in the Dutch East Indies in 1913, the amount available for exports has decreased, although not in proportion to the increase in the amount of coconut oil. (P. 344)

A description of the mining of **potash** in Germany is given. (P. 346)

A lack of coal is limiting the production of the Belgian **glass industries.** (P. 352)

Sulfuric acid is much in demand in Belgium. (P. 352)

Artificial silk production is increasing in Belgium but is still inadequate to meet more than a fraction of the demand. (P. 352)

Tanned hides are finding good demand in Belgium despite the high prices. (P. 352)

The **iron-ore** resources of Canada are described and the following table is given showing the total shipments of iron ore from all the mines of Canada and of the United States from 1913 to 1918, inclusive:

Calendar Year	Canadian Mines Short Tons	United States Mines Short Tons	Calendar Year	Canadian Mines Short Tons	United States Mines Short Tons
1913.....	307,634	69,418,089	1916....	275,176	87,215,019
1914.....	244,854	46,412,532	1917....	215,302	84,641,992
1915.....	398,112	62,152,272	1918....	211,608	80,663,746

(Pp. 353–4)

It is generally conceded that **oil** is the future fuel of Italy and coöperative fuel-oil purchasing societies are proposed. (Pp. 354–5)

Thirty-five towns in Thuringia have organized for the purchase and development of **peat beds** lying in the Weser Basin, south of Bremen. (P. 362)

The following table shows the **cottonseed products** manufactured, shipped out, and on hand in the United States from August 1, 1919, to March 31, 1920:

Items	Year	On Hand Aug. 1	Produced Aug. 1 to Mar. 31	Shipped out Aug. 1 to Mar. 31	On Hand Mar. 31
Crude oil, lbs.	1920	25,495,597	1,118,690,109	1,016,198,606	142,724,123[1]
	1919	16,503,655	1,106,807,412	983,069,401	166,093,276
Refined oil, lbs.	1920	148,488,608[2]	816,664,592[3]	....	348,890,856[2]
	1919	265,875,255	830,895,057	....	301,087,328
Cake and meal, tons	1920	44,548	1,681,185	1,458,197	267,536
	1919	28,751	1,838,935	1,767,607	100,079
Hulls, tons	1920	124,593	1,035,832	1,051,934	108,491
	1919	60,425	928,359	808,864	179,920
Linters, 500-pound bales	1920	254,616	569,816	556,001	268,431
	1919	30,868	835,789	580,973	285,684
Hull fiber, 500-pound bales	1920	52,119	137,396	27,204	162,311
	1919	11,609	109,174	89,059	31,724
Grabbots, motes, etc., 500-pound bales	1920	11,134	17,460	15,894	12,700
	1919	12,453	22,718	17,880	17,291

[1] Includes 12,542,914 and 7,738,405 lbs. held by refining and manufacturing establishments and 7,209,350 and 26,750,882 lbs. in transit to refiners and consumers Aug. 1 and Mar. 31, respectively.

[2] Includes 4,569,701 and 16,138,735 lbs. held by refiners brokers, agents, and warehousemen at places other than refineries and manufacturing establishments and 7,614,431 and 10,680,510 lbs. in transit to manufacturers of lard substitute, oleomargarine, soap, etc., Aug. 1 and Mar. 31, respectively.

[3] Produced from 934,531,010 lbs. crude oil.

(P. 455)

During the fiscal year ended March 31, 1919, the United States imported into Siam **chemicals** and **medicines** valued at $33,256, lubricating oil, $46,634, metal manufactures, $619,963, mineral oil, $284,188, paints, $10,785, paper and manufactures, $48,649, rubber goods, $29,531, and zinc, $30,340. (P. 365)

The situation in the German **paper-making** industry is unsatisfactory. The high rate of exchange prevented the importation of cellulose, and the cost of pulp made from native wood has greatly increased. (P. 372)

The South China **paper-making** industry has suffered greatly and the import trade in paper has thrived. (Pp. 388–9)

There is said to be a market in Japan for the following articles: **stearine, paraffin,** and **olein; drugs;** and **dyes,** such as direct black, acid black, and the basic colors, malachite green, menthyl violet, and auramine. (Pp. 394–5)

Annually, on a normal basis, the **textile industries** of Poland require, in addition to the principal dyes, the following:

	Tons		Tons
Gum tragacanth	100	Nitric acid	50
Gum de cordofane	50	Acetic acid	1,000
Bleaching powder	1,000	Yellow glycerol	40
Sulfate of soda (calcined)	7,500	White glycerol	100
Caustic soda	6,000	Stearine	20
Carbonate of soda (calcined)	3,500	Coconut oil	500
Acetate of soda	200	Cottonseed oil	550
Bichromate of potash or of soda	600	Castor oil	450
Ferrocyanide of potash or of soda	100	Olein (for soaps and softenings)	3,300
Chlorate of potash or of soda	60	Tallow	3,400
Chromium acetate (dry)	20	Cachou de gambir ou pegne	20
Nitrate of soda	50	Campeche, dry, American	200
Tannin	50	Haematein crystals	100
Double salt of antimony	50	Persian berry	20
Chrome alum	250	Quercitron extract	100
Alum or sulfate of aluminum	200	Aniline salt	200
Hydrosulfite (for printing)	10	Aniline oil	20
Bisulfite of soda (dry)	200	Paranitraniline	100
Bisulfite of potash	500	β-naphthol	100
Copper sulfate	60	α-naphthylamine	30
Sulfuric acid	6,000	Sodium sulfide	3,200
Hydrochloric acid	2,000	Sulfur	1,000

(P. 400)

The following figures give some idea of the increase in the **productive** capacity of France during the war in **chemical** substances other than fine chemicals:

	1913		1919	
Products	Production Tons	Consumption Tons	Production Tons	Consumption Tons
Sulfuric acid, 58°	1,160,000	1,172,500	2,500,000	1,500,000
Sulfuric acid, 66°	58,000	58,000	1,200,000	.....
Oleum (fuming sulfuric acid)	6,000	6,000	300,000	25,000
Nitric acid	20,000	18,500	360,000	20,000
Sodium salts	625,500	506,000	800,000	650,000
Liquid chlorine	300	.....	90,000	15,000
Bromine	.....	100	500	200
Calcium carbide	32,000	28,000	200,000	.....
Calcium cyanamide	7,500	8,000	300,000	.....
Ammonium salts	75,000	95,000	200,000	150,000
Nitrate of lime	.....	9,500	250,000	250,000
Natural phosphates	2,700,000	1,220,000	3,000,000	2,700,000
Superphosphates	1,965,000	1,900,000	2,500,000	2,500,000
Phosphorus	300	30	3,600	.....

Great strides have also been made in the manufacture of synthetic products, an impetus having been given by the requirements of the war. (P. 441)

Arrangements have been concluded for the Rumanian government to pay for American railway equipment in **petroleum.** (P. 369)

On March 1, 1920, the Mexican Ministry of Industry, Commerce, and Labor formally inaugurated an **industrial experimental laboratory** in connection with the commercial museum. (P. 404)

The foreign trade in **news-print paper** and **paper-making materials** is reviewed. (Pp. 435–41)

A market for American **leathers** in France is reported. (Pp. 456–7)

The total value of the **minerals** produced in the Union of South Africa during the closing 6 mo. of 1919 amounted to $96,826,209. This is an increase of $287,917 as compared with the value of the corresponding output in 1918, but is a decrease of $3,583,193 as compared with that of the first 6 mo. of that year. (P. 475)

The discovery of rich **copper** deposits in the southern part of the island of Timor, Dutch East Indies, is reported. (P. 478)

The scarcity and high prices of **battick dyes** has so affected the industry in Java that many of the smaller concerns have been forced to stop work. The shortages of indigo and of alizarin red are the most acute. (P. 478)

An order has been issued prohibiting the importation into Gambia of all **dyestuffs** which are not the produce or manufacture of the British Empire. (P. 481)

The Anglo-Danubian Association plans to supply **raw materials** to the industrials of former Austrian states. (P. 481)

A growing demand for **cement** in India is reported. (P. 510)

The Chinese **oil** and **oil-yielding nut** and seed industries are reviewed. (Pp. 519–22)

Conditions in the German **paper** industry at the beginning of 1920 were worse than they had previously been. (P. 525)

A syndicate has been formed in Austria to establish a large scale **chemical** undertaking. The output is to be confined at first to sulfuric acid, caustic soda, and alcohol for other chemical products, but as the company expands it is planned to manufacture other products, such as hydrochloric acid, potassium permanganate, and a large number of pharmaceutical products. The power for the enterprise will be obtained from the abundant water supply. (P. 607)

Statistics are given showing the Russian exports of seeds before the war. (Pp. 530–1)

The **wood pulp** and **paper** markets of Norway continue to be firm with prices soaring. (P. 549)

Italy's **paper** industry has been severely affected by the cutting off of large imports of cellulose which were formerly supplied by Germany and Austria. (P. 555)

The **wood-distillation** industry of Canada is reviewed. (P. 631)

SPECIAL SUPPLEMENTS ISSUED

UNITED KINGDOM—*22b* CHINA—*55b*

NEW PUBLICATIONS

By Clara M. Guppy, Librarian, Mellon Institute of Industrial Research, Pittsburgh

Atomic Theory: Development of the Atomic Theory. A. N. Meldrum. 13 pp. Price, 1s. 6d. Oxford University Press.

Beverages: Homemade Beer and Wine. Howard Williams. 190 pp. Price, $1.50. E. A. Cook, 26 Van Buren St.., Chicago, Ill.

Bismuth: Bismuth, Etain, Plomb. A. Bouchonnet. 375 pp. Price, 7 fr. 50. O. Doin et Fils, Paris.

Cement. B. Blount, W. H. Woodcock and H. J. Gillett. Price, 18s. Longmans, Green & Co., London.

Chemical Industries of German Rhineland; A Summary of the Report of the British Chemical Mission on Chemical Factories in the Occupied Area of Germany. 29 pp. Association of British Chemical Manufacturers, London.

Chemistry, Inorganic. 2d Ed. Translated from the 4th Revised and Amplified Italian Edition by T. H. Pope. Ettore Molinari. Vol. 1. 867 pp. Price, £2 2s. J. & A. Churchill, London.

Chemistry: Everyday Chemistry. Alfred Vivian. 12 mo. 560 pp. Price, $1.64. American Book Co., New York.

Chemistry: Industrial Organic Analysis. P. S. Arup. 2d Ed. Revised and Enlarged. 471 pp. Price, 12s. 6d J. & A. Churchill, London.

Chemistry: Introduction to General Chemistry. H. N. McCoy and E. M. Terry. 8 vo. 605 pp. Price, $3.00. McGraw-Hill Book Co., New York.

Chemistry: Laboratory Manual of Elementary Colloid Chemistry. Emil Hatschek. 8vo. 135 pp. Price, 6s. 6d. J. & A. Churchill, London.

Chemistry: Treatise on General and Industrial Inorganic Chemistry. Ettore Molinari. 2d Ed. Translated by T. H. Pope. 8vo. Price, 42s. J. & A. Churchill, London.

Chemistry: Volumetric Analysis. J. B. Coppock. 2d Ed. Revised and Enlarged. 8vo. 100 pp. Price, 3s. 6d. Sir Isaac Pitman & Sons, London.

Coal: Chemistry of Coal. J. B. Robertson. 96 pp. Price, 3s. 6d. Gurney & Jackson, London.

Cobalt, Nickel, and the Elements of the Platinum Group. J. N. Friend. 8vo. 384 pp. Price, 18s. Charles Griffin & Co., London.

Einstein's Theory of Gravitation, The Foundations of. Authorized English Translation by H. L. Brose. Preface by Albert Einstein. Erwin Freundlich. 8vo. 77 pp. Price, 5s. Cambridge University Press.

Electric Furnaces in the Iron and Steel Industry. Translated from the original and now completely rewritten. William Rodenhauser and Others. 3d Ed. Revised 8vo. 460 pp. Price, $4.50. John Wiley & Sons, Inc., New York.

Food Inspection and Analysis. A. E. Leach and A. L. Winton. 4th Ed. Revised and Enlarged. 1090 pp. Price, $8.50. John Wiley & Sons, Inc., New York.

Fuel Production and Utilization. H. S. Taylor. 8vo. 297 pp. Price, 10s. 6d. Baillière, Tindall & Cox, London.

Glass Manufacture. Walter Rosenhain. 2d Ed. 258 pp. Price, 12s. 6d. Constable & Co., London.

Industrial Research: Organization of Industrial Scientific Research. C. E. K. Mees. 8vo. 175 pp. Price, $2.00. McGraw-Hill Book Co., New York.

Iron and Steel: The A B C of Iron and Steel; with a Directory of the Iron and Steel Works and Their Products of the United States and Canada. A. O. Backert, Editor. 3d Ed. 8vo. 375 pp. Price, $5.00. Penton Pub. Co., Cleveland.

Manganese Ores. A. H. Curtis. 118 pp. Price, 3s. 6d. John Murray, London.

Paper-Making and Its Machinery. T. W. Chalmers. 189 pp. Price, 26s. Constable & Co., London.

Petroleum: A Handbook of Petroleum, Asphalt and Natural Gas, Methods of Analysis, Specifications, Properties, Refining Processes, Statistics, Tables and Bibliography. Roy Cross. 2d Ed. 12mo. 496 pp. Price, $5.00. Kansas City Testing Laboratory, Kansas City.

Saccharine: Ueber die Kontrolle und Herstellung von Saccharin. Oskar Beyer. 141 pp. Rascher & Cie, Zurich.

Technical Writing. T. A. Rickard. 12mo. 178 pp. Price, $1.50. John Wiley & Sons, Inc., New York.

RECENT JOURNAL ARTICLES

Acetic Acid: Synthetic Acetic Acid and Acetone. Description of the Process and Method of Production of Acetic Acid, Acetates and Acetone from Calcium Carbide. J. T. Rooney. *Chemical and Metallurgical Engineering*, Vol. 22 (1920), No. 18, pp. 847–850.

Asbestos, A Canadian Specialty. F. C. C. Lynch *Mining and Scientific Press*, Vol. **120** (1920), No. 15, pp. 531–533.

Catalyzer: A New Type of Catalyzer for Hydrogenation; Description of a Method of Preparing Finely Divided Nickel Catalyzer by Mechanical Grinding. W. D. Richardson. *Chemical and Metallurgical Engineering*, Vol. 22 (1920), No. 17, pp. 793–796.

Cellulose: The Reactions of Cellulose. J. E. Minor. *Paper*, Vol. 26 (1920), No. 8, pp. 16–19.

Coal-tar Products Used in Rubber Industry. Frederick Dannerth. *Color Trade Journal*, Vol. 6 (1920), No. 4, pp. 113–116.

Colloidal Fuel and Its Use. L. W. Bates. *The Chemical Engineer*, Vol. 28 (1920), No. 3, p. 73.

Ethylene and Propylene Chlorhydrins and Glycols from Oil Gas. B. T. Brooks. *Chemical and Metallurgical Engineering*, Vol. 22 (1920), No. 14, pp. 629–633.

Ferrite: Genesis of Ferrite. Federico Giolitti. *Chemical and Metallurgical Engineering*, Vol. 22 (1920), No. 16, pp. 737–739.

Fuels: A Method of Determining the Relative Temperatures of Spontaneous Ignition of Solid Fuels. F. S. Sinnatt and Burrows Moore. *Journal of the Society of Chemical Industry*, Vol. 39 (1920), No. 6, pp. 72*t*–78*t*.

Gasoline Production and Substitutes. E. W. Dean. *Chemical Age*, Vol. 2 (1920), No. 3, pp. 423–426.

Glass: Science and the Glass Industry. C. H. Kerr. *The Chemical Engineer*, Vol. 28 (1920), No. 4, pp. 107–111.

Limestone Analysis: Limestone Examination and Evaluation for Bisulfite Liquor Manufacture. W. E. B. Baker. *Paper*, Vol. 26 (1920), No. 7, pp. 70–88.

Lubrication: The Theory and Practice of Lubrication: The "Germ" Process. H. M. Wells and J. E. Southcombe. *Journal of the Society of Chemical Industry*, Vol. 39 (1920), No. 5, pp. 51*t*–60*t*.

Microscopy and Biology in Industry. F. A. Mason. *The Chemical Age* (London), Vol. 2 (1920), No. 44, pp. 396–399.

Microscopy of Pulpwoods; The Structure of Woods Used in the Pulp and Paper Industry. Eloise Gerry. *Paper*, Vol. 26 (1920), No. 7, pp 19–34.

Nickel Coinage; A Comparison of Nickel with Other Metals for Coinage. Advantages of Nickel Coinage. A. E. MacDonald. *Canadian Chemical Journal*, Vol. 4 (1920), No. 4, pp. 106–108.

Nitrate Industry in Chile; Geography, Geology and Economic Situation of Chilean Nitrate. Alejandro Bertrand. *Chemical and Metallurgical Engineering*, Vol. 22 (1920), No. 14, pp. 655–659.

Nitrogen: Method of Fixing Nitrogen and Status of Processes throughout the World. A. H. White. *Chemical Age*, Vol. 2 (1920), No. 4. pp 447–450.

Oil Shale Industry: Present Status of the Oil Shale Industry. V. C. Alderson. *Chemical Age*, Vol. 2 (1920), No. 3, pp. 427–430.

Paints: Analysis of Paints and Varnishes. A. De Waele. *The Chemical Age* (London), Vol. 2 (1920), No. 44, pp. 406–407.

Petroleum Distillation Described. Expert Refiner Tells of Methods Generally Used in Obtaining Various Products from Crude. H. J. Struth. *The Oil and Gas Journal*, Vol. 18 (1920), No. 47, p. 70.

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Producer Gas as Fuel for the Glass Industry. F. J. Denk. *Journal of the American Ceramic Society*, Vol. 3 (1920), No. 2, pp. 94–113.

Radium: The Story of Radium. How Luminous Metals and Million-Dollar Remedies Are Put within the Use of All. H. A. Mount. *Scientific American*, Vol. 122 (1920), No. 17, pp. 454–468.

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Salt Production and Trade of the United States. J. V. Meigs. *Chemical Age*, Vol. 2 (1920), No. 2, pp. 391–396.

Sewage Purification: Activated Sludge Process of Sewage Purification—Large-Scale Operation. Edward Ardern. *Journal of the Society of Chemical Industry*, Vol. 39 (1920), No 5, pp. 60*t*–64*t*.

Steel: A Comparative Test upon High-Speed Steels. A. J. Langhammer. *Chemical and Metallurgical Engineering*, Vol. 22 (1920), No. 18, pp. 829–832.

Sugar: A Survey of the World's Sugar Situation. Howaro Elliott. *Chemical Age*, Vol. 2 (1920), No. 4, pp. 451–452.

Sulfur Dyes: Application of Sulfur Dyes. Emile Cagliostro. *Color Trade Journal*, Vol. 6 (1920), No 4, pp. 120–124.

Tannins: The Synthetic Tannins and Their Use in Tanning; Efforts to Replace the Natural Vegetable Product. Ed. Nihoul. *Scientific American Monthly*, Vol. 1 (1920), No. 4, pp. 326–330.

Tungsten: Le Tungstene Minerais, Métallurgie, Propriétés et Applications. Camille Matignon. *Chimie et Industrie*, Vol. 3 (1920), No. 3, pp. 277–292.

MARKET REPORT—MAY, 1920

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

		May 1	May 15
Acid, Boric, cryst., bbls.	lb.	$.16\frac{1}{2}$	$.16\frac{1}{2}$
Hydrochloric, com'l, 22°	lb.	.03	$.03\frac{1}{2}$
Hydriodic	oz.	.19	.19
Nitric, 42°	lb.	$.08\frac{1}{2}$	$.08\frac{1}{2}$
Phosphoric, 50% tech	lb.	.25	.25
Sulfuric, C. P.	lb.	.07	.07
Chamber, 66°	ton	22.00	22.00
Oleum	ton	27.00	28.00
Alum, ammonia, lump	lb.	.04	.04
Aluminum Sulfate (iron-free)	lb.	.03	$.03\frac{1}{2}$
Ammonium Carbonate, pwd.	lb.	$.13\frac{1}{2}$	$.14\frac{1}{2}$
Ammonium Chloride, gran.	lb.	.18	.18
Ammonia Water, carboys, 26°	lb.	.10	.10
Arsenic, white	lb.	.14	.15
Barium Chloride	ton	175.00	175.00
Nitrate	lb.	.11	.11
Barytes, white	ton	30.00	30.00
Bleaching Powd., 35%, Works,	100 lbs.	5.50	5.50
Borax, cryst., bbls.	lb.	$.09\frac{1}{2}$	$.09\frac{1}{2}$
Bromine, tech., bulk	lb.	.85	.85
Calcium Chloride, fused	ton	25.00	27.50
Chalk, precipitated	lb.	.05	.05
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	8.25	8.25
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.25	1.25
Iodine, resublimed	lb.	4.35	4.35
Lead Acetate, white crystals	lb.	.15	.15
Nitrate	lb.	.15	.15
Red American	100 lbs.	$.10\frac{1}{2}$	$.10\frac{1}{2}$
White American	100 lbs.	$.09\frac{1}{2}$	$.09\frac{1}{2}$
Lime Acetate	100 lbs.	3.50	3.50
Lithium Carbonate	lb.	1.50	1.50
Magnesium Carbonate, Tech	lb.	.12	.12
Magnesite	ton	65.00	65.00
Mercury flask	75 lbs.	85.00	95.00
Phosphorus, yellow	lb.	.35	.35
Plaster of Paris	100 lbs.	1.50	1.50
Potassium Bichromate	lb.	.40	.40
Bromide, Cryst	lb.	.90	.95
Carbonate, calc., 80–85%	lb.	.22	.22
Chlorate, cryst	lb.	.15	.15
Cyanide, bulk, 98–99%	lb.	.30	.30
Hydroxide, 88–92%	lb.	.30	.30
Iodide, bulk	lb.	3.35	3.35
Nitrate	lb.	.14	.14
Permanganate, U. S. P.	lb.	.90	.90
Salt Cake	ton	30.00	32.00
Silver Nitrate	oz.	.68	.63
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	3.65	3.65
Caustic, 76%	100 lbs.	6.50	6.50
Sodium Acetate	lb.	.12	.12
Bicarbonate	100 lbs.	2.75	3.00
Bichromate	lb.	.40	.33
Chlorate	lb.	.10	.10
Cyanide	lb.	.27	.27
Fluoride, technical	lb.	.18	.18
Hyposulfite	100 lbs.	3.60	3.60
Nitrate, 95%	100 lbs.	3.85	3.90
Silicate, 40°	lb.	.02	.02
Sulfide	lb.	.08	.09
Bisulfite, powdered	lb.	$.06\frac{1}{2}$	$.06\frac{1}{2}$
Strontium Nitrate	lb.	.27	.27
Sulfur, flowers	100 lbs.	3.75	3.75
Crude	long ton	30.00	30.00
Talc, American, white	ton	20.00	20.00
Tin Bichloride	lb.	$.21\frac{1}{2}$	$.21\frac{1}{2}$
Oxide	lb.	.60	.60
Zinc Chloride, U. S. P.	lb.	.50	.50
Oxide, bbls.	lb.	.22	.22

ORGANIC CHEMICALS

		May 1	May 15
Acetanilid	lb.	.75	.75
Acid, Acetic, 28 p. c.	100 lbs.	3.60	4.00
Glacial	lb.	$.17\frac{1}{2}$	.17
Acetylsalicylic	lb.	.95	1.95
Benzoic, U. S. P., ex-toluol	lb.	.85	.85
Carbolic, cryst., U. S. P., drs.	lb.	.15	.15
50- to 110-lb. tins	lb.	.21	.23
Acid (*Concluded*)			
Citric, crystals, bbls.	lb.	1.17	1.15
Oxalic, cryst., bbls.	lb.	.55	.58
Pyrogallic, resublimed	lb.	2.50	2.50
Salicylic, bulk, U. S. P.	lb.	.55	.55
Tartaric, crystals, U. S. P.	lb.	.83	.83
Trichloracetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.21	.22
Alcohol, denatured, 190 proof	gal.	1.03	1.13
Ethyl, 190 proof	gal.	7.00	7.00
Wood, Pure	gal.	3.50	3.50
Amyl Acetate	gal.	4.00	4.00
Camphor, Jap. refined	lb.	2.00	2.10
Carbon Bisulfide	lb.	.07	.08
Tetrachloride	lb.	$.11\frac{1}{2}$	$.12\frac{1}{2}$
Chloroform, U. S. P.	lb.	.35	.35
Creosote, U. S. P.	lb.	.75	.75
Cresol, U. S. P.	lb.	.18	.18
Dextrine, corn	lb.	$.06\frac{1}{4}$	$.06\frac{1}{4}$
Imported Potato	lb.	.14	.14
Ether, U. S. P., conc., 100 lbs	lb.	.21	.21
Formaldehyde	lb.	.60	.58
Glycerin, dynamite, drums	lb.	.23	$.24\frac{1}{2}$
Pyridine	gal.	3.50	3.50
Starch, corn	100 lbs.	5.25	5.25
Potato, Jap.	lb.	.06	.06
Rice	lb.	.25	.25
Sago	lb.	.05	.05

OILS, WAXES, ETC.

		May 1	May 15
Beeswax, pure, white	lb.	.65	.65
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	.18	.18
Ceresin, yellow	lb.	.14	.14
Corn Oil, crude	lb.	.16	.16
Cottonseed Oil, crude, f. o. b. mill	lb.	$.15\frac{1}{2}$	.16
Menhaden Oil, crude (southern)	gal.	.85	.85
Neat's-foot Oil, 20°	gal.	2.25	2.25
Paraffin, 128–130 m. p., ref.	lb.	$.11\frac{1}{2}$	$.11\frac{1}{2}$
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs.	bbl.	19.75	20.25
Rosin Oil, first run	gal.	.90	.90
Shellac, T. N.	lb.	1.30	1.10
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.95	1.95
Stearic Acid, double-pressed	lb.	$.27\frac{1}{2}$	$.27\frac{1}{2}$
Tallow Oil, acidless	gal.	1.60	1.60
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	nominal	2.45

METALS

		May 1	May 15
Aluminum, No. 1, ingots	lb.	.32	.32
Antimony, ordinary	100 lbs.	9.75	9.75
Bismuth	lb.	2.52	2.52
Copper, electrolytic	lb.	$.18\frac{1}{2}$	.19
Lake	lb.	$.18\frac{3}{4}$	.19
Lead, N. Y.	lb.	$.08\frac{1}{2}$	$.08\frac{1}{2}$
Nickel, electrolytic	lb.	.45	.45
Platinum, refined, soft	oz.	155.00	115.00
Quicksilver, flask	75 lbs ea.	85.00	95.00
Silver	oz.	1.18	1.08
Tin	lb.	$.62\frac{1}{2}$	$.62\frac{1}{2}$
Tungsten Wolframite	per unit	7.00	7.00
Zinc, N. Y.	100 lbs.	8.00	7.75

FERTILIZER MATERIALS

		May 1	May 15
Ammonium Sulfate	100 lbs.	7.10	7.10
Blood, dried, f. o. b. N. Y.	unit	8.00	8.00
Bone, 3 and 50, ground, raw	ton	48.00	48.00
Calcium Cyanamide, unit of Ammonia		4.00	4.00
Fish Scrap, domestic, dried, f. o. b. works	unit	7.25	7.25
Phosphate Rock, f. o. b. mine:			
Florida pebble, 68%	ton	6.85	6.85
Tennessee, 78–80%	ton	11.00	11.00
Potassium muriate, 80%	unit	2.60	2.50
Pyrites, furnace size, imported	unit	.18	.18
Tankage, high-grade, f. o. b. Chicago	unit	7.75	7.75

COAL-TAR CHEMICALS

		May 1	May 15
Crudes			
Benzol, C. P.	gal.	.33	.33
Cresol, U. S. P.	lb.	.18	.18
Naphthalene, flake	lb.	.15	.14
Phenol, drums	lb.	.15	.15
Toluol, 90%	gal.	.34	.34
Xylol, water white	gal.	.40	.40
Intermediates			
Acids:			
Anthranilic	lb.	2.75	2.75
B	lb.	2.25	2.25
Benzoic	lb.	.85	.85
Broenner's	lb.	1.75	1.75
Cleves	lb.	2.00	2.00
Cresylic, 97–99%	gal.	1.00	1.10
F	lb.	3.00	3.50
Gamma	lb.	2.50	2.50
H	lb.	1.85	2.25
Metanilic	lb.	1.70	1.70
Monosulfonic F	lb.	3.00	3.50
Napthionic, crude	lb.	1.10	1.10
Neville & Winther's	lb.	1.90	1.90
Phthalic	lb.	.60	.60
Picric	lb.	.25	.25
Sulfanilic	lb.	.35	.35
Tobias'	lb.	2.25	2.25
Amido Azo Benzol	lb.	1.15	1.15
Aniline Oil	lb.	.35	.35
For Red	lb.	.65	.65
Aniline Salt	lb.	.47	.47
Anthracene, 80–85%	lb.	.75	.75
Anthraquinone	lb.	4.50	4.50
Benzaldehyde, tech	lb.	.75	.75
U. S. P.	lb.	1.25	1.00
Benzidine Base	lb.	1.40	1.40
Benzidine Sulfate	lb.	1.15	1.15
Diamidophenol	lb.	6.00	6.00
Dianisidine	lb.	9.00	9.00
p-Dichlorbenzol	lb.	.10	.10
Diethylaniline	lb.	1.40	1.40
Dimethylaniline	lb.	1.45	1.45
Dinitrobenzol	lb.	.36	.36
Dinitrotoluol	lb.	.43	.43
Diphenylamine	lb.	.80	.80
G Salt	lb.	.90	.90
Hydroquinone	lb.	2.00	2.00
Metol	lb.	11.50	11.50
Monochlorbenzol	lb.	.15	.15
Monoethylaniline	lb.	2.15	2.15
a-Naphthylamine	lb.	.45	.45
b-Naphthylamine	lb.	1.15	1.15
b-Naphthol, crude	lb.	.80	.85
m-Nitraniline	lb.	1.00	1.00
p-Nitraniline	lb.	1.65	1.75
Nitrobenzol, crude	lb.	.16	.16
Rectified (Oil Myrbane)	lb.	.18	.18
p-Nitrophenol	lb.	.80	.80
p-Nitrosodimethylaniline	lb.	1.90	1.90
o-Nitrotoluol	lb.	.25	.22
p-Nitrotoluol	lb.	1.50	1.15
m-Phenylenediamine	lb.	1.35	1.35
p-Phenylenediamine	lb.	2.65	2.65
Phthalic Anhydride	lb.	.45	.45
Primuline Base	lb.	3.00	3.00
R Salt	lb.	.90	.90
Resorcin, tech	lb.	4.00	4.00
U. S. P.	lb.	6.00	6.00
Schaeffer Salt	lb.	.75	.75
Sodium Naphthionate	lb.	1.10	1.10
Thiocarbanilid	lb.	.60	.60
Tolidine, Base	lb.	1.75	1.65
Toluidine, mixed	lb.	.44	.44
o-Toluidine	lb.	.35	.35
m-Toluylenediamine	lb.	1.35	1.35
p-Toluidine	lb.	1.75	2.00
Xylidene, crude	lb.	.45	.45

COAL-TAR COLORS

		May 1	May 15
Acid Colors			
Black	lb.	1.15	1.15
Blue	lb.	3.00	3.00
Acid Colors (*Concluded*)			
Fuchsin	lb.	4.25	4.25
Orange III	lb.	1.00	1.00
Red	lb.	1.10	1.10
Violet 10B	lb.	6.50	6.50
Alkali Blue, domestic	lb.	4.75	4.75
Imported	lb.	8.00	8.00
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	2.00	2.00
Erythrosine	lb.	12.00	12.00
Indigotine, conc	lb.	3.00	3.00
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.50	1.50
Ponceau	lb.	1.25	1.35
Scarlet 2R	lb.	1.00	1.00
Direct Colors			
Black	lb.	1.00	1.00
Blue 2B	lb.	.70	.70
Brown R	lb.	1.80	1.80
Fast Red	lb.	3.50	3.50
Yellow	lb.	2.00	2.00
Violet, con't	lb.	2.20	2.20
Chrysophenine, domestic	lb.	2.25	2.25
Imported	lb.	3.80	3.80
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00
Oil Colors			
Black	lb.	.70	.70
Blue	lb.	1.65	1.65
Orange	lb.	1.40	1.40
Red III	lb.	1.65	1.65
Scarlet	lb.	1.75	1.75
Yellow	lb.	1.70	1.70
Nigrosine Oil, soluble	lb.	.90	.90
Sulfur Colors			
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.90	.90
Chrome Colors			
Alizarin Blue, bright	lb.	7.75	7.75
Alizarin Red, 20% Paste	lb.	1.10	1.10
Alizarin Yellow G	lb.	1.00	1.00
Chrome Black, domestic	lb.	1.25	1.25
Imported	lb.	2.20	2.20
Chrome Blue	lb.	2.50	2.50
Chrome Green, domestic	lb.	1.50	1.50
Chrome Red	lb.	2.00	2.00
Gallocyanine	lb.	3.25	3.25
Basic Colors			
Auramine, O, domestic	lb.	2.50	2.50
Auramine, OO,	lb.	4.15	4.15
Bismarck Brown Y	lb.	.90	.90
Bismarck Brown R	lb.	1.20	1.20
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	6.00	6.00
Indigo, 20 p. c. paste	lb.	.85	.85
Fuchsine Crystals, domestic	lb.	5.00	5.50
Imported	lb.	12.00	12.00
Magenta Acid, domestic	lb.	4.25	4.25
Malachite Green, crystals	lb.	3.75	3.75
Methylene Blue, tech	lb	2.50	2.75
Methyl Violet 3 B	lb	2.60	2.60
Nigrosine, spts. sol	lb.	.85	.85
Water sol., blue	lb.	.65	.65
Jet	lb	.90	.90
Phosphine G., domestic	lb.	7.00	7.00
Rhodamine B ex-con't	lb.	35.00	35.00
Victoria Blue, base, domestic	lb	6.00	6.00
Victoria Green	lb	6.00	6.00
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00

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